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Temperature Dependence of Carbonate Radical in $NaHCO_3$ and Na_2CO_3 Solutions: Is the Radical a Single Anion?

Guozhong Wu, Yosuke Katsumura,* Yusa Muroya, Mingzhang Lin, and Tomomi Morioka

Nuclear Engineering Research Laboratory, School of Engineering, The University of Tokyo,
Shirakata Shirane 2−22, Tokai-mura, Naka-gun, Ibaraki 319-1188, Japan

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The carbonate radical was investigated by pulse radiolysis in both $NaHCO_3$ and Na_2CO_3 solutions over 15−400 °C. There was almost no change in the absorption spectrum of the carbonate radical within the temperature range studied. However, the absorbance of carbonate radical increased with temperature for $NaHCO_3$ solution at any concentration considered, whereas the absorbance for Na_2CO_3 solution increased with temperature at high concentrations and decreased at low concentrations $\leq 2 \times 10^{-3}$ m (mol/kg). The second-order rate constant for the decay of the carbonate radical exhibited a complicated temperature dependence: it decreased with temperature up to about 120 °C, and then it slowly increased with temperature up to 300 °C followed by a rapid increase with temperature at 300−400 °C. The decay was also dependent on the concentration of $NaHCO_3$ or Na_2CO_3. If considering the carbonate radical as $CO_3^{\bullet-}$, the experimentally measured yield was always smaller than the simulated one, and the discrepancy was enlarged at lower carbonate/bicarbonate concentrations. We propose that the carbonate radical is present in the form of a dimer anion, either $(CO_3)_2^{\bullet 3-}$ or $H(CO_3)_2^{\bullet 2-}$. The equilibrium constants for the formation of $(CO_3)_2^{\bullet 3-}$ and $H(CO_3)_2^{\bullet 2-}$ were obtained for various temperatures. The measured radical yield can correlate well with the simulated result using the dimer model. We further estimated pK_a of $H(CO_3)_2^{\bullet 2-}$ at temperatures up to 250 °C. The pK_a at 25 °C was 9.30±0.15, in good agreement with the literature value of 9.5−9.6 obtained by measuring the pH dependence of the reactivity.

Introduction

Interests in the chemistry of supercritical or high-temperatured water are continuously growing due to its intrinsic thermodynamic and physical properties[1−4] and applications in many industrial fields.[5−8] Pulse radiolysis and laser photolysis can be employed to study the consequences of the changes of water properties on radical reactions occurring in the compressible region by monitoring the time-dependent optical absorption of the target species on a very short time scale. For that purpose, hydrated electron (e_{aq}^-) and $OH^\bullet$ generated from water radiolysis may be used as sensitive probes. Studies of e_{aq}^- in high-temperature[9−11] and supercritical water[12,13] revealed the significant red-shifting of the absorption peak and the broadening of the spectrum with increasing temperature, indicating a shallower potential well for e_{aq}^- at high temperatures. In contrast with the e_{aq}^-, direct measurement of $OH^\bullet$ radical is difficult because its absorption band is in the ultraviolet region and the maximum absorption coefficient is small (ϵ^{188}=540 $M^{-1}cm^{-1}$ at room temperature[14]). Therefore, $OH^\bullet$-derived radicals such as $(SCN)_2^{\bullet-}$ and carbonate radical, formed via one-electron oxidation of the corresponding ions, can be used as an alternative approach. In a previous paper on $(SCN)_2^{\bullet-}$,[15] it was revealed that the absorption spectrum red-shifted and the decay was accelerated over the temperature range of 25−400 °C. From the KSCN concentration dependence of the $(SCN)_2^{\bullet-}$ yield, the equilibrium constant for $(SCN)_2^{\bullet-}$ was found to decrease with temperature. It was concluded that the $(SCN)_2^{\bullet-}$, less stable in high temperature water, is inappropriate to evaluate the dose of electron beam, although 0.01 M KSCN solution is widely used as the standard reference for pulse radiolysis at room temperature. This paper reports our recent work on temperature dependence of carbonate radical, which is one of the most extensively studied inorganic radicals.

The importance of studying the temperature effects on carbonate radical is manifold. In the first place, if the carbonate radical is stable in supercritical water and its molar absorption coefficient is established, one is able to evaluate the $OH^\bullet$ radical yield, which is important to the design of supercritical water-cooled nuclear reactor.[16] This new type of reactor is believed to have higher operating efficiency and profitability, and its design is in progress.[17,18] Second, as in the case of H_2O_2-mediated destruction of organic compounds in subcritical and supercritical water, $OH^\bullet$ and $HO_2^\bullet$ radicals are thought to be intermediates[19,20] and can react with bicarbonate and carbonate ions to produce carbonate radicals. The bicarbonate and carbonate ions are deprotonated from H_2CO_3 because carbon dioxide is the major oxidation product and is partly converted in water to H_2CO_3. Although carbonate radical reacts more slowly than $OH^\bullet$ with most organic substrates, it is nonetheless a strong oxidant with a reduction potential of 1.50−1.59V vs NHE.[21,22] It is of importance to study the kinetics of its reactions with various substrates in high-temperature region.[23] Third, a detailed study of the carbonate radical at high temperatures may provide new insights into the understanding of its structure and pH dependence because the available results in the literature obtained at room temperature contain conflicting evidence[24,25] regarding the protonation state. A reasonable explanation to the conflicts is important for both fundamental understanding and

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* To whom correspondence should be addressed. The Nuclear Engineering Research Laboratory, School of engineering, The University of Tokyo, Hongo 7-3-1, Bunkyo-ku, Tokyo 113, Japan. Fax/telephone: +81-3-5841-8624. Email: katsu@q.t.u-tokyo.ac.jp.

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other aspects including biology,[26,27] waste and drinking water treatment,[28,29] evaluation of the influence of nuclear waste on groundwater,[30,31] and so forth. Because bicarbonate ions are abundantly present in biological systems,[32] and carbonate/bicarbonate ions are present in natural water and groundwater, H_2O_2-derived or radiation-induced $OH^•$ radical can be transformed to the carbonate radical that is supposed to act as a chain carrier.

Owing to the decrease of dielectric constant and H-bond of water with temperature, the carbonate radical will experience a very different local solvation in high-temperature water than in room-temperature water. This altered structure might have a significant effect on the properties of carbonate radical. In this work, pulse radiolysis technique was applied to examine the behavior of the carbonate radical in $NaHCO_3$ and Na_2CO_3 solutions as a function of solute concentration and temperature over 15−400 °C. The results demonstrate that the absorption spectrum is almost independent of temperature, whereas the self-decay rate constant exhibits a complicated temperature dependence. The temperature dependence of the radical yield is quite different between $NaHCO_3$ and Na_2CO_3 solutions. We propose that the carbonate radical probably exists in the form of a dimer anion, $(CO_3)_2^{•3-}$ or $H(CO_3)_2^{•2-}$, formed by the coupling of $CO_3^{•-}$ with carbonate or bicarbonate ion. This is reasonably in analogy with other dimer radical anions of the $X_2^{•-}$ (X = Cl, Br, I, SCN) type. The equilibrium constants for the formation of $(CO_3)_2^{•3-}$ and $H(CO_3)_2^{•2-}$ at various temperatures were obtained. pK_a of $H(CO_3)_2^{•2-}$ as a function of temperature was also established. The validity of the dimer anion model was verified by the simulation using the available parameters.

Experimental Section

A flowing cell for high-temperature pulse radiolysis was used and its details were described elsewhere.[12,33] Sapphire windows were used for the access of analyzing light and the optical path was 1.5 cm. A pulsed Xenon lamp (5 μs) was used to measure the absorption spectra, whereas a He−Ne laser (633 nm) was used to observe the formation and decay of the carbonate radical. The pulse width of electron beam was 50 ns, delivered from a 35 MeV linac at the University of Tokyo. The dose per pulse ranged from 20 to 35 Gy, determined by using N_2O-saturated 0.01 M KSCN solution and $G\epsilon = 5.2 \times 10^{-4}$ m^2/J at 472 nm[34] at room temperature. Absorbed doses were corrected for the variation of water density with temperature. Stock 0.1 m (mol/kg) $NaHCO_3$ and 0.1 m Na_2CO_3 solutions were prepared, respectively, by dissolving the solutes in Millipore filtered water. Solutions at various concentrations were prepared by the dilution of the stock solutions. All the solutions were purged with N_2O in order to rapidly convert e_{aq}^- into $OH^•$, and the solution flow rate was 3−5 mL/min. Experiments were performed over the temperature range of 15−400 °C, but in many cases the temperature used was not higher than 300 °C to reduce the corrosive nature of the alkaline solution.[35] It was found that the sapphire windows, after being in contact with the basic solution above 300 °C for a long time, turned opaque due to the corrosion, and the light transmittance was drastically attenuated.

Results

Formation Rate of the Carbonate Radical. Under our experimental conditions, the carbonate radical was produced by the oxidation of CO_3^{2-} or HCO_3^- with $OH^•$ radical

$$OH^• + HCO_3^- \rightarrow H_2O + CO_3^{•-} \tag{1}$$

$$OH^• + CO_3^{2-} \rightarrow OH^- + CO_3^{•-} \tag{2}$$

The rate constant can be obtained by tracking the buildup of absorption due to carbonate radical, and k_2 is known to be 40−50 times higher than k_1 under standard conditions. In this work, k_1 was measured over 25−320 °C with the use of 0.4−2 × 10^{-2} M (cold) $NaHCO_3$ solutions. No correction was made for the change of HCO_3^- concentration at high temperature due to the hydrolysis of HCO_3^-. Figure 1 shows that log k_1 is linearly proportional to $1/T$ up to 320 °C, and this result is in good agreement with the work of Buxton et al.[36] except for the value at 25 °C. The slightly higher k_1 at 25 °C measured in our work is due to the pH rise caused by the saturation of bicarbonate solution with N_2O.[37] For the determination of k_2 at high temperature, hydrolysis of CO_3^{2-} has to be taken into account. As k_2 has been measured by Buxton et al.[36] at temperatures up to 200 °C, no attempt was made here to measure k_2 at higher temperature. It is because almost all of the CO_3^{2-} ions will be hydrolyzed to HCO_3^- at temperatures above 200 °C if the initial concentration of Na_2CO_3 is not high. As also shown in Figure 1, there is little change in the apparent rate constant with temperature for the carbonate radical formation in 1 × 10^{-3} m Na_2CO_3, and the value at higher temperature is close to that for the reaction with $NaHCO_3$ as a result of the hydrolysis.

Buxton et al.[36] suggested that the reactions of $OH^•$ with CO_3^{2-} and HCO_3^- have the same activation energy, and the difference in their rate constants occurs mainly in the Arrhenius preexponential factors. The higher k_2 than k_1 may reflect the greater resonance in CO_3^{2-} because the oxidation is supposed[38] to proceed via the addition of $OH^•$ to the C=O group. By assuming the same activation energy for the reactions of $OH^•$ with HCO_3^- and CO_3^{2-}, k_1 and k_2 as a function of $1/T$ can be given as follows

$$\log k_1 = 11.18 - 1.24 \times 10^3/T \tag{3}$$

$$\log k_2 = 12.77 - 1.24 \times 10^3/T \tag{4}$$

where T is the Kelvin temperature. As shown in Figure 1, k_1 predicted from eq 3 is slightly higher than the measured one. The predicted k_1 may be closer to the real value if one considers the fact that the hydrolysis of HCO_3^- to H_2CO_3 is favored at high temperature and the reaction of $OH^•$ with H_2CO_3 may be much slower[24] than with HCO_3^-.

Decay of the Carbonate Radical. The decay of the carbonate radical at room temperature is relatively slow,[39,40] with a rate constant of 1.4 × 10^7 M^{-1}s^{-1}. A negative temperature dependence of the decay was previously observed[41,42] at temperatures below 70 °C. Recently, Ferry and Fox[23] determined the decay rate constant in 9.4 × 10^{-3} M Na_2CO_3 (cold) solution over 25−400 °C. They found that the decay reaction had a small negative temperature dependence at low temperatures but a great positive temperature dependence at temperatures higher than 300 °C. For a better understanding of the mechanism of the decay, the decay rate constants were measured over a wide temperature range in $NaHCO_3$ and Na_2CO_3 solutions with various concentrations.

Figure 2 shows time-dependent profiles of the carbonate radical at 633 nm for $NaHCO_3$ and Na_2CO_3 solutions at 15−300 °C. There is little change in the profile from 15 to 150 or 200 °C but the decay is slightly faster at 300 °C. However, the decay at 400 °C (not shown) is remarkably faster than at lower temperatures. The second-order decay rate constants are obtained

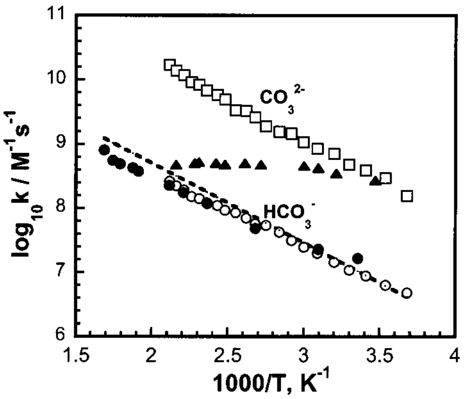

Figure 1. Arrhenius plots for the reactions of OH• radical with HCO_3^- (k_1) and CO_3^{2-} (k_2). ○ k_1 (Buxton et al.[36]); ● k_1 (this work, P = 250 atm)); - - - - k_1 (expected values using the same activation energy as for k_2); □ k_2 (Buxton et al.[36]); ▲ the apparent rate constant for solution with initial concentration of 1 × 10^{-3} m Na_2CO_3 (P = 250 atm).

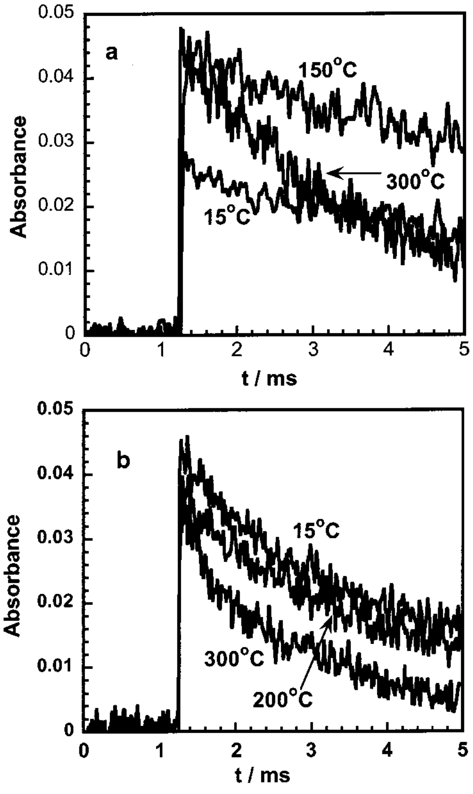

Figure 2. Time profiles of the carbonate radical in (a) 2 × 10^{-2} m $NaHCO_3$ and (b) 5 × 10^{-3} m Na_2CO_3 solutions at 250 atm. N_2O-saturated, dose = 30 Gy per pulse.

by assuming that the absorption coefficient of carbonate radical is independent of temperature and its value at 633 nm is 85% (1700 $M^{-1}cm^{-1}$) of that at 600 nm. As seen in Figure 3, for both $NaHCO_3$ and Na_2CO_3 solutions, the rate constant decreases slightly with temperature and then tends to increase at temperatures above 150 °C. The rate constant increases drastically above 300 °C and the value at 400 °C is about 2 orders of magnitude higher. In addition, the decay rate constant near 400 °C seems to be independent of the solute concentration. There is a similarity in temperature dependence of the radical decay between Na_2CO_3 and $NaHCO_3$ solutions. Our results for solutions with 0.01−0.1 m concentrations are in good agreement with the work of Ferry and Fox [23] on 9.4 × 10^{-3} M (cold) Na_2CO_3 solution.

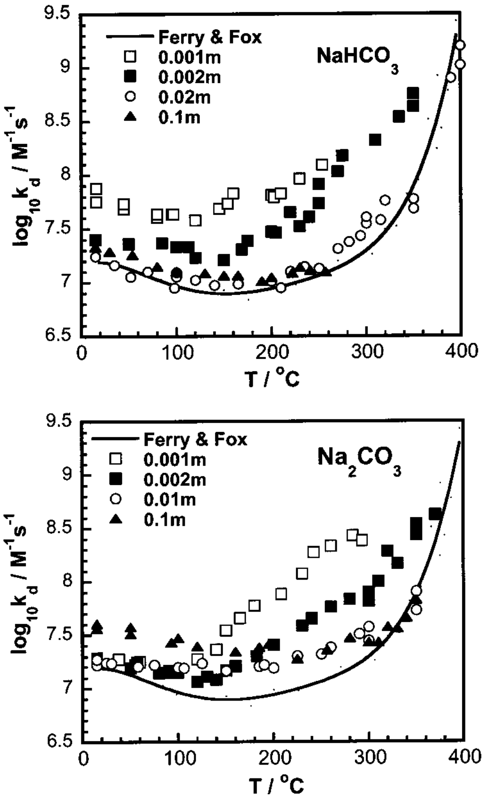

Figure 3. Temperature dependence of the second-order decay rate constant of the carbonate radical in $NaHCO_3$ and Na_2CO_3 solutions (up to 300 °C, P = 250 atm; higher than 300 °C, P = 350 atm). The solid line was taken from the work of Ferry and Fox[23] on 9.4 × 10^{-3} M (cold) Na_2CO_3 solution (P = 282 atm).

It is also of particular interest to notice the concentration effects on the decay rate constant. For Na_2CO_3 solutions, the decay at 0.1 m is obviously faster than at 0.01 m up to 150 °C due to the ionic strength effect. However, the rate constant is identical at 0.01−0.1 m concentrations above 200 °C. For $NaHCO_3$ solutions, the decay rate constant is identical at 0.01−0.1 m concentrations and no ionic strength effect is identified over the temperature range investigated, in accordance with the early work at room temperature.[42] The difference in the concentration dependence between $NaHCO_3$ and Na_2CO_3 solutions is in good agreement with Chen et al.[25] These authors observed at room temperature that the reactions of the carbonate radical with substrates at pH 7 was independent of ionic strength in contrast to the ionic strength effect at pH 12. For solutions with concentrations lower than 0.01 m, the decay reaction has an inverse concentration dependence. As also seen in Figure 3, the decay rate constants for 1 × 10^{-3} m and 2 ×10^{-3} m Na_2CO_3 solutions above 200 °C are considerably higher than for concentrated Na_2CO_3 solutions; whereas the values for 1 × 10^{-3} and 2 ×10^{-3} m $NaHCO_3$ solutions are always higher than concentrated solutions from room temperature to high temperature. However, the rate constants approach the same when temperature is near 400 °C, being independent of solute concentration. At temperatures higher than 200 °C, the decay behavior in Na_2CO_3 solution with concentration below 0.01 m is very similar to that in $NaHCO_3$ solution under similar conditions. This is because there is little difference in solution property between dilute $NaHCO_3$ and Na_2CO_3 solutions at high temperature as most of the CO_3^{2-} ions are transformed to HCO_3^- ions as the result of the favored hydrolysis.

Temperature Dependence of Absorption Spectrum. At room temperature, the carbonate radical has a broad absorption

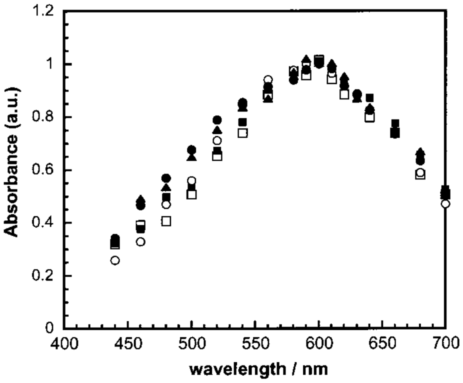

Figure 4. Normalized absorption spectra of the carbonate radical in 0.1 m Na_2CO_3 solution at various temperatures. N_2O-saturated, dose = 35 Gy per pulse. □ 25 °C, 200 atm; ■ 100 °C, 200 atm; ○ 200 °C, 200 atm; ● 300 °C, 250 atm ($d = 0.745$ g/cm^3); ▲ 400 °C, 350 atm ($d = 0.473$ g/cm^3).

with λ_{max} of 600 nm and ϵ_{max} of 1934−2000 M^{-1}cm^{-1}.[43−45] Figure 4 shows normalized absorption spectra recorded at 25−400 °C in 0.1 m Na_2CO_3 solution. No obvious changes in spectral shape and absorption peak were observed with increasing temperature, although the spectral width seems to be slightly broadened at high temperatures. It appears that the absorption peak in the short wavelength side shifts slightly to shorter wavelength, whereas the one in the long wavelength side seems to remain unvaried with temperature. These findings are consistent with previous reports on the spectrum at high temperature. McCracken and Buxton[38] confirmed that the spectrum was independent of temperature up to 200 °C, and Elliot et al.[43] further observed a slight difference in spectrum between 20 °C and 300 °C with λ_{max} shifting from 600 to 595 nm. Elliot et al.[43] also found that the spectra were identical for the carbonate radical in both light and heavy water up to 300 °C. Compared with the substantial red-shifting of spectrum observed for e_{aq}^{-} [12,13] and $(SCN)_2^{\bullet-}$ [15], the nearly invariant absorption spectrum up to 400 °C is indicative of the higher stability of the carbonate radical. Absorption coefficient of the carbonate radical is assumed to be constant with temperature.

Concentration Dependence of Absorbance. Due to the small ϵ_{max} of the carbonate radical and the relatively low rate constant for the oxidation of carbonate or bicarbonate ion by $OH^{\bullet}$ radical, concentrated $NaHCO_3$ or Na_2CO_3 solutions (≥10 mM) are usually applied in pulse radiolysis experiment. Because the yield of carbonate radical increases with temperature, it can be used to indirectly measure the $OH^{\bullet}$ radical in the radiolysis of high-temperature water. In the present work, the concentration dependence of the absorbance at 633 nm was examined by varying the $NaHCO_3$ and Na_2CO_3 concentrations from 0.1 m to very low values. One can calculate the yield of carbonate radical from the absorbance by using ϵ_{633} and the optical length. As shown in Figure 5a, the absorbance in $NaHCO_3$ solution increases with increasing temperature for any concentration, and the temperature effect is more pronounced at lower concentrations. However, as shown in Figure 5b, the temperature dependence of the absorption of the carbonate radical in Na_2CO_3 solution is not uniform for various concentrations. It is interesting to note that the absorbance decreases with temperature for 5×10^{-4} to 2×10^{-3} m Na_2CO_3 solutions. This is the first observation of a negative temperature dependence for the absorbance of carbonate radical. At high Na_2CO_3 concentrations, the absorbance always increases with temperature and the variation of concentration appears to have little influence on the absorbance-temperature relationship.

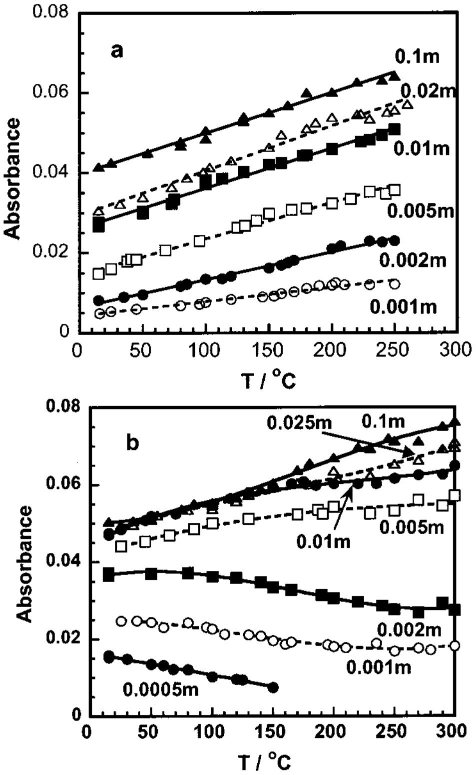

Figure 5. Variation of absorbance at 633 nm with temperature for the carbonate in (a) $NaHCO_3$ and (b) Na_2CO_3 solutions. N_2O-saturated, dose = 30 Gy/pulse, $P = 250$ atm. The water density was normalized to 1.0 g/cm^3.

The difference in temperature dependence of absorbance between Na_2CO_3 and $NaHCO_3$ solutions may be attributed to the lower reactivity of the $OH^{\bullet}$ radical with HCO_3^{-} than that with CO_3^{2-} and the change of dissociation constant with temperature for HCO_3^{-} and CO_3^{2-} ions. For confirmation, the total carbonate radical yield, $CO_3^{\bullet-}{}_T$, was simulated for temperatures from 25 to 250 °C and compared with the experimental values under identical conditions. The dissociation constants of carbonic acid and other rate constants of the reactions involved are presented in Table 1. No simulation was made for temperatures higher than 250 °C because the first and second dissociation constants of carbonic acid are available only for temperatures below 200 °C. In the simulation, temperature dependence of the $OH^{\bullet}$ yield in N_2O-saturated water was assumed to be the same as that of the total yield of e_{aq}^{-} and $OH^{\bullet}$ in N_2-saturated water. Figures 6 and 7 show the simulated and experimental results for $NaHCO_3$ and Na_2CO_3 solutions at various temperatures. It is shown that only at high concentrations the simulated results are well consistent with the experimental data. At lower concentrations, the simulated yield is higher than the measured one for any concentrations and temperatures considered. This is not possibly due to the inaccuracy of the parameters involved, because the rate and the dissociation constants for room temperature are well established.

Discussions

Model of the Carbonate Radical. Early studies have shown that, on the basis of the pH dependence of the rate constants for reactions with inorganic and organic solutes, the acid−base equilibrium of the carbonate radical was supposed to be

$$H^{+} + CO_3^{\bullet-} \rightleftarrows HCO_3^{\bullet} \qquad (5)$$

TABLE 1: Parameters Used for the Calculation of HCO_3^- and CO_3^{2-} Concentrations and for the Simulation of the $CO_3^{\bullet-}$ Yield

reaction[a]	formula[b]	reference
	calculation of the real HCO_3^- and CO_3^{2-} concentrations	
$H_2O \rightleftarrows OH^- + H^+$	$pK_w = 3.74 + 3050/T - 14.8\log_{10}\rho_w$	Quist (1970)[46]
$H_2CO_3^- \rightleftarrows H^+ + HCO_3^-$	$pK_{1d} = -1234.4 + 68608/T + 193.4\ln(T) -0.1642T - 3.747 \times 10^6/T^2$	Park et al. (1998)[47]
$HCO_3^- \rightleftarrows H^+ + CO_3^{2-}$	$pK_{2d} = -14.44 + 5.188 \times 10^{-2}T - 3.27 \times 10^{-5}T^2 + 3644.8/T$	Patterson et al. (1984[c])[48]
	simulation of the $CO_3^{\bullet-}$ yield	
$OH^\bullet + OH^\bullet \rightarrow H_2O_2$	$\log_{10}(2k) = 11.02 - 399.9/T$	Elliot (1994)[49]
$OH^\bullet + CO_3^{2-} \rightarrow OH^- + CO_3^{\bullet-}$	$\log_{10}k = 12.77 - 1.24 \times 10^3/T$	Buxton et al. (1988)[36]
$OH^\bullet + HCO_3^- \rightarrow H_2O + CO_3^{\bullet-}$	$\log_{10}k = 11.18 - 1.24 \times 10^3/T$	Buxton et al. (1988)[36] and this work
G-value of $OH^\bullet$ in N_2O-saturated water (μmol/J)	$G(OH^\bullet)^d = 0.619 + 1.259 \times 10^{-3}t$	Elliot (1994)[49]

[a] Units: $M^{-1}\ s^{-1}$ for rate constants, $(mol\ kg^{-1})^2$ for K_w, and $mol\ kg^{-1}$ or $kg\ mol^{-1}$ for equilibrium constants. [b] T is the Kelvin temperature, t is the Celsius temperature, and ρ is the water density ($kg\ dm^{-3}$). [c] The formula was obtained by fitting the experimental data as shown in the paper. [d] G-values of e_{aq}^- and $OH^\bullet$ as a function of temperature are taken from Elliot,[49] and multiplied by the factor $G(OH^\bullet)_{N2O}/((G(e_{aq}^-)+G(OH^\bullet))_{N2} = 1.15$ obtained at room temperature.

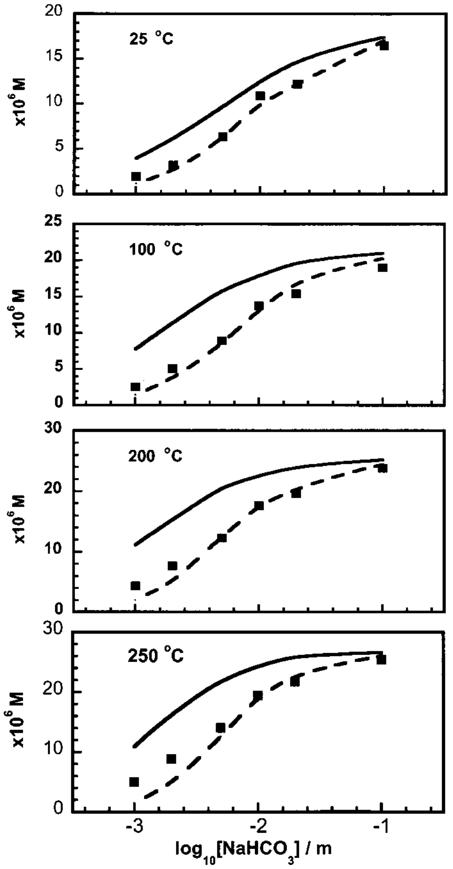

Figure 6. Comparison of the simulated and measured yields for the carbonate radical in $NaHCO_3$ solutions from 25 to 250 °C. Conditions are the same as shown in Figure 5. Solid line: based on the $CO_3^{\bullet-}$ model; dashed line: based on the dimer model; ■ experimental results.

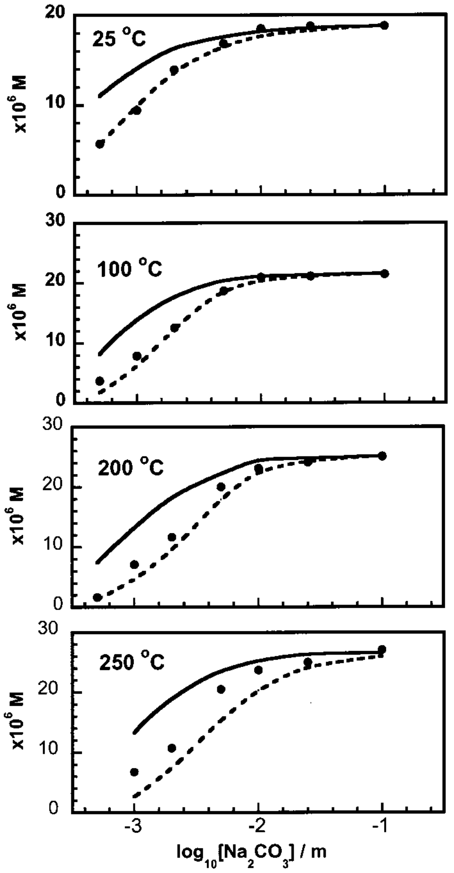

Figure 7. Comparison of the simulated and measured yields for the carbonate radical in Na_2CO_3 solutions from 25 to 250 °C. Conditions are the same as shown in Figure 5. Solid line: based on the $CO_3^{\bullet-}$ model; dashed line: based on the dimer model; ■ experimental results.

The pK_a of bicarbonate radical was previously determined to be 9.6 ± 0.3,[25,50] 9.5 ± 0.2,[44] or 7.0−8.2[41] at room temperature. However, more recently, Czapski et al.[24] found no pH dependence of the absorption spectrum of the carbonate radical over the pH range of 2.7−10.0. They speculated that in analogy with HNO_3 and H_2SO_4, the $HCO_3^\bullet$ should be a strong acid with $pK_a < 0$, based on the fact that all of these species are of the same type: $XO_n(OH)_m$ (X = C, N, S). In addition, the Raman spectra at pH 7.5−12.3[51] and ESR spectra at pH 7.5−11.9[52] did not show any obvious change with pH, indicating no protonation of the carbonate radical above pH 7.5. Further work[45] stresses that the pH dependence of the carbonate radical reactivity toward some inorganic ions observed at high ionic strength[44] might be relevant to the medium effects, i.e., the composition of ions in solution, instead of the dissociation of $HCO_3^\bullet$. However, although no spectral change for the carbonate radical as a function of pH was observed, some evidence (if not all) of the pH effect on its reactivity is indisputable. For example, the rate constant for the reactions with substrates was found to be independent of ionic strength at pH 7, whereas it showed a positive dependence on $\mu^{1/2}$ at pH 12.[50] Our investigations on the temperature dependence of the decay and the absorbance also indicate that the nature of the carbonate radical is somewhat different in $NaHCO_3$ and $NaCO_3$ solutions.

TABLE 2: Equilibrium Constants of Dimeric Carbonate Radical Obtained by Regression and the Calculated pK_a of $H(CO_3)_2^{\bullet 2-}$

T °C	$[NaHCO_3]^a$ 10^{-3}m	$[Na_2CO_3]^a$ 10^{-3}m	$[HCO_3^-]/[CO_3^{2-}]^b$ –	[dimer]/$[CO_3^{\bullet -}]$ –	K_1 m^{-1}	K_2 10^3 m^{-1}	pK_a m
25	1−10	0.5−2	90−0.2	0.9−2.5	330 ± 50	3.70 ± 0.45	9.30 ± 0.15
50	1−10	0.5−2	120−1.0	0.8−3.4	390 ± 50	3.62 ± 0.16	9.22 ± 0.13
100	1−10	0.5−2	240−5.9	0.5−3.4	320 ± 40	7.62 ± 0.52	8.75 ± 0.12
150	1−10	0.5−5	420−15.5	0.6−10.7	330 ± 60	6.99 ± 0.54	8.94 ± 0.18
200	1−10	0.5−5	830−30	0.6−9.5	380 ± 50	20.45 ± 1.67	8.76 ± 0.14
250	1−10	1−5	1280−140	1.0−6.6	530 ± 50	[c]	

[a] Initial molal concentration of the solute. [b] Calculated based on the first and second dissociation constants of carbonic acid. [c] Not regressed with the variable $[CO_3^{2-}]$ because it is too small as compared to $[HCO_3^-]$.

To explain the above-mentioned conflicting evidence on the carbonate radical, we propose that the carbonate radical occurs in a dimeric form produced via the following processes

$$CO_3^{\bullet -} + HCO_3^- \leftrightharpoons H(CO_3)_2^{\bullet 2-} \text{ (in NaHCO}_3\text{ solution) } K_1 \quad (6)$$

$$CO_3^{\bullet -} + CO_3^{2-} \leftrightharpoons (CO_3)_2^{\bullet 3-} \text{ (in Na}_2\text{CO}_3\text{ solution) } K_2 \quad (7)$$

Under the standard conditions, the carbonate radical can be present in the form of either $(CO_3)_2^{\bullet 3-}$ or $H(CO_3)_2^{\bullet 2-}$ or both, depending on the pH. The observation of a lack of spectral change with pH is due to the fact that the "H" atom is located far from the unpaired electron. It is most likely that the acidic and basic forms of the dimeric carbonate radical are transformed by

$$H(CO_3)_2^{\bullet 2-} \rightleftarrows H^+ + (CO_3)_2^{\bullet 3-} \; K_a \quad (8)$$

Therefore, the pK_a of 9.5−9.6[25,44,50] previously determined for the assumed $HCO_3^{\bullet}$ at room temperature is actually the value for $H(CO_3)_2^{\bullet 2-}$. As will be shown, its pK_a can be predicted on the basis of a series of equilibrium constants with regard to the carbonate radical.

The proposed dimer model for the carbonate radical in analogy with radicals having the type $X_2^{\bullet -}$ (X = Cl, Br, I, SCN) is more reasonable than the speculation[24] in analogy with acids having the $XO_n(OH)_m$ type, because the formation route and the oxidizing property of the carbonate radical are very similar to $X_2^{\bullet -}$ radicals. According to our model, the pH dependence of the reactivity of the carbonate radical is due to the difference in the oxidizing capability between $(CO_3)_2^{\bullet 3-}$ and $H(CO_3)_2^{\bullet 2-}$, rather than the transformation of $CO_3^{\bullet -}$ to $HCO_3^{\bullet}$. However, if the concentration of CO_3^{2-} or HCO_3^- is very low, reactions 6 and 7 may proceed mainly to the left and the concentration of $CO_3^{\bullet -}$ could be higher than that of the dimer radical anion.

Equilibrium Constants and pK_a of the Carbonate Radical. In principle, the equilibrium constant K_1 and K_2 for $H(CO_3)_2^{\bullet 2-}$ and $(CO_3)_2^{\bullet 3-}$ as a function of temperature can be investigated based on the general equation

$$A_\infty/A = 1 + \{1/(K[\text{solute}])\} \quad (9)$$

where A_∞ is the absorbance per unit dose for $(CO_3)_2^{\bullet 3-}$ or $H(CO_3)_2^{\bullet 2-}$ when all the $CO_3^{\bullet -}$ radicals are converted to dimer radical anions, and A is the absorbance of unit dose at a certain concentration of CO_3^{2-} or HCO_3^-. However, due to the fact that both CO_3^{2-} and HCO_3^- are always present in solution and the rate constants for their reactions with $OH^{\bullet}$ radical are quite different, eq 9 is inapplicable to the determination of K_1 or K_2.

Under conditions where equilibria 6−7 are established

$$[H(CO_3)_2^{\bullet 2-}] + [(CO_3)_2^{\bullet 3-}] = [CO_3^{\bullet -}]_e(K_1[HCO_3^-] + K_2[CO_3^{2-}]) \quad (10)$$

By rearranging the equation, we get

$$[\text{dimer}]/[CO_3^{\bullet -}]_e = K_1[HCO_3^-] + K_2[CO_3^{2-}] \quad (11)$$

Or in the form

$$[\text{dimer}]/([CO_3^{\bullet -}]_T - [\text{dimer}]) = K_1[HCO_3^-] + K_2[CO_3^{2-}] \quad (12)$$

where $[CO_3^{\bullet -}]_e$ is the concentration at equilibrium and $[CO_3^{\bullet -}]_T$ is the total concentration of carbonate radical. [dimer] is the sum of the concentrations of $[H(CO_3)_2^{\bullet 2-}]$ and $[(CO_3)_2^{\bullet 3-}]$. $[CO_3^{\bullet -}]_T$ under a certain condition can be calculated by taking into account the reactions of CO_3^{2-} and HCO_3^- with $OH^{\bullet}$ radical and the self-recombination of $OH^{\bullet}$ radicals. The real concentrations of CO_3^{2-} and HCO_3^- for Na_2CO_3 or $NaHCO_3$ solutions are calculated based on the first and second dissociation constants of carbonic acid and the ionic product of water. By assuming that the absorption coefficient is the same for $H(CO_3)_2^{\bullet 2-}$ and $(CO_3)_2^{\bullet 3-}$ at 633 nm and the $CO_3^{\bullet -}$ has no absorption at this wavelength, the [dimer] can be calculated from the absorbance by taking the $\epsilon_{633} = 1700$ M^{-1} cm^{-1} and optical length = 1.5 cm. Because a series of data were available for each temperature, the equilibrium constants K_1 and K_2 can be obtained by regression in accordance with eq 12. The results are presented in Table 2.

Both K_1 and K_2 increase with temperature, but K_2 is 10 times higher than K_1. This is consistent with the higher absorbance observed in Na_2CO_3 solution than in $NaHCO_3$ solution under otherwise identical conditions. Using the obtained K_1 and K_2 values, the total yield of $H(CO_3)_2^{\bullet 2-}$ and $(CO_3)_2^{\bullet 3-}$ as a function of $NaHCO_3$ or Na_2CO_3 concentration was calculated for different temperatures and compared with the experimental data. As shown in Figures 6 and 7, the simulated curves using the dimer model are in good agreement with the experimental data for $NaHCO_3$ and Na_2CO_3 solutions with any concentration over 25−200 °C. There is a discrepancy at 250 °C for solutions with low concentrations, probably due to either the uncertainty in the first and second dissociation constants of carbonic acid or underestimated value of K_1.

From the known K_1 and K_2 values, one is able to derive the pK_a of the carbonate radical. Under conditions where equilibrium (8) is established

$$K_a = \frac{[H^+][(CO_3)_2^{\bullet 3-}]}{[H(CO_3)_2^{\bullet 2-}]} = \frac{[(CO_3)_2^{\bullet 3-}]}{[CO_3^{\bullet -}][CO_3^{2-}]} \times \frac{[CO_3^{\bullet -}][HCO_3^-]}{[H(CO_3)_2^{\bullet 2-}]} \times \frac{[H^+][CO_3^{2-}]}{[HCO_3^-]} = K_1K_2^{-1}K_{2d} \quad (13)$$

From logarithm of both sides of the equation, we get

$$pK_a = pK_1\text{-}pK_2 + pK_{2d} \quad (14)$$

K_{2d} is the second dissociation constant of carbonic acid, and pK_{2d} values at higher temperature have been determined by Patterson et al.[48] and Park et al.[53] There is almost no difference between their values for temperatures below 100 °C, but an apparent difference exists above 150 °C. The data of Patterson et al. were applied in this work and further extrapolated to 250 °C. The calculated pK_a values at temperatures of 25−200 °C are also listed in Table 2. It is very interesting that our calculated pK_a at room temperature is 9.30 ± 0.15, in good agreement with the value of 9.5−9.6 determined by the pH "titration" method. The pK_a decreases slightly with temperature and then begins to increase with temperature. The temperature dependence of the pK_a is similar to that of the first and second dissociation constants of carbonic acid.[47,48,53]

Although one of our major motivations for studying the carbonate radical is to determine radiolysis yields of $OH^{\bullet}$ radical at high temperatures, the equilibrium behavior of carbonate radical and the hydrolysis of carbonate ions make the system not simple as we expected. Because the yield of carbonate radical at high temperatures is strongly dependent on the $NaHCO_3$ or Na_2CO_3 concentration, it seems unsuitable to take the carbonate radical yield under a certain condition as the $OH^{\bullet}$ yield. However, the yields of $OH^{\bullet}$ radical at high temperatures may be measured by the use of high concentrated Na_2CO_3 solution. More work is still needed to study the concentration dependence of carbonate radical at 300−400 °C with the use of sapphire window that is more resistant to the basic solution.

Explanation to the Decay Behavior. The concentration dependence of the overall decay cannot be explained by the model of single radical anion ($CO_3^{\bullet-}$). However, it can be explained well by the dimer model. Taking the $(CO_3)_2^{\bullet 3-}$ in Na_2CO_3 solution as an example and neglecting the presence of $H(CO_3)_2^{\bullet 2-}$, the radical decays through the following processes

$$(CO_3)_2^{\bullet 3-} + (CO_3)_2^{\bullet 3-} \rightarrow \text{product} \qquad (15)$$

$$(CO_3)_2^{\bullet 3-} + CO_3^{\bullet -} \rightarrow \text{product} \qquad (16)$$

$$CO_3^{\bullet -} + CO_3^{\bullet -} \rightarrow \text{product} \qquad (17)$$

The overall rate constant for the second-order decay is

$$k_{obs} = 2k_{15} + 2k_{16}/K_2' + 2k_{17}/K_2'^2 \qquad (18)$$

where $K_2' = K_2[CO_3^{2-}]$. At a fixed temperature, the equilibrium constant K_2 is constant, and the overall decay of $(CO_3)_2^{\bullet 3-}$ is dependent on carbonate concentration. At high concentrations where $K_2[CO_3^{2-}]$ is much larger than unit, the self-combination of $(CO_3)_2^{\bullet 3-}$ is predominant, and k_{obs} is equal to $2k_{15}$. At very low concentrations, the concentration of $CO_3^{\bullet -}$ could be as high as that of $(CO_3)_2^{\bullet 3-}$, so the decay is faster with decreasing the carbonate concentration, as already shown in Figure 3b. The decay of $H(CO_3)_2^{\bullet 2-}$ in $NaHCO_3$ solutions can be similarly explained.

To explain the negative temperature dependence of the decay rate constant, a dimerization model of $CO_3^{\bullet -}$ was previously proposed[41] as given below

$$CO_3^{\bullet -} + CO_3^{\bullet -} \rightleftarrows C_2O_6^{2-} \rightarrow C_2O_4^{2-} + O_2 \qquad (19)$$

By assuming that the equilibrium is exothermic and the equilibrium constant is less than unit, the apparent activation energy for the decay can therefore become negative. Although this mechanism works well for the decay in the low-temperature range, it cannot explain the positive temperature dependence observed at higher temperature. More recently, the analysis of products in irradiated carbonate solution showed[54] that the yield of oxalate ion was less than 1% of the total yield of carbonate radical. We propose that the abnormally small temperature dependence of the decay up to about 300 °C is due to the acidic-basic equilibrium of the dimeric carbonate radical. A rise in temperature leads to the change in the concentrations of CO_3^{2-} and HCO_3^-, but the stability of the carbonate radical is less altered because $CO_3^{\bullet -}$ can couple with either CO_3^{2-} or HCO_3^- to form dimeric carbonate radical. The negative temperature dependence at lower temperature and the positive temperature dependence above 150 °C for the decay are in accordance with the temperature dependence of the dissociation constants of H_2CO_3 and HCO_3^- over this temperature range. At temperature higher than 300 °C, very high pK_a values of H_2CO_3 and HCO_3^- are expected and no CO_3^{2-} will be present in solution. Therefore, the carbonate radical is only in the form of $H(CO_3)_2^{\bullet 2-}$, and its decay should increase with temperature. This explains the remarkable increase of the decay rate with temperature above 300 °C as compared to lower temperatures. Another explanation[23] for the fast decay above 300 °C, especially at temperatures near 400 °C, is the clustering of the carbonate radical. Owing to the substantial decrease of dielectric constant and the collapse of hydrogen-bond network near the critical temperature of water, the carbonate radical may be present in the form of $[Na^+\text{-}H(CO_3)_2^{\bullet 2-}]$ or $[Na_22+\text{-}H(CO_3)_2^{\bullet 2-}]$ ion pair. Taking an example, the excited sate of the naphtholate-potassium ion pair was observed in KOH solution even at 200 °C.[55] The clustering of the carbonate radical leads to a higher local concentration of reactive radicals than their apparent bulk concentration, the decay is hence favored.

Formation Rate Constants. Because the rate constants for the reactions of $OH^{\bullet}$ with CO_3^{2-} and HCO_3^- are usually derived by considering the carbonate radical as $CO_3^{\bullet -}$, it is required to clarify whether these rate constants still remain valid if the carbonate radical is actually $(CO_3)_2^{\bullet 3-}$ or $H(CO_3)_2^{\bullet 2-}$.

By neglecting the HCO_3^- formed by the hydrolysis of CO_3^{2-}, the total yield of $(CO_3)_2^{\bullet 3-}$ and $CO_3^{\bullet -}$ radicals in Na_2CO_3 solution at time t equals the amount of $OH^{\bullet}$ radicals disappeared

$$[(CO_3)_2^{\bullet 3-}]_t + [CO_3^{\bullet -}]_t = [OH^{\bullet}]_0 - [OH^{\bullet}]_t = [OH]_0(1 - \exp(-k_2't)) \qquad (20)$$

Under conditions where all the $OH^{\bullet}$ radicals are disappeared, then

$$[(CO_3)_2^{\bullet 3-}]_{inf} + [CO_3^{\bullet -}]_{inf} = [OH]_0 \qquad (21)$$

where subscripts 0, t, and inf denote concentrations at time zero, t, and infinite, and k_2' is equal to $k_2[CO_3^{2-}]$.

From eqs 20−21, we get

$$\ln \frac{[(CO_3)_2^{\bullet 3-}]_{inf} + [CO_3^{\bullet -}]_{inf}}{([(CO_3)_2^{\bullet 3-}]_{inf} + [CO_3^{\bullet -}]_{inf}) - ([(CO_3)_2^{\bullet 3-}]_t - [CO_3^{\bullet -}]_t)} = - \ln \frac{[OH]_0}{[OH]_0 - [OH]_0(1 - \exp(-k_2't))} = - \ln \exp(-k_2't) = k_2't \qquad (22)$$

Under conditions where equilibrium 7 is displaced to the right, $[(CO_3)_2^{\bullet 3-}]$ is much larger than $[CO_3^{\bullet -}]$, then eq 22 can be simplified to

$$\ln \frac{[(CO_3)_2^{\bullet 3-}]_{inf}}{[(CO_3)_2^{\bullet 3-}]_{inf} - [(CO_3)_2^{\bullet 3-}]_t} = k_2{}'t \qquad (23)$$

However, if $(CO_3)_2^{\bullet 3-}$ is not present or $[CO_3^{\bullet -}] \gg [(CO_3)_2^{\bullet 3-}]$, eq 23 becomes the form usually cited in the literature

$$\ln \frac{[CO_3^{\bullet -}]_{inf}}{[CO_3^{\bullet -}]_{inf} - [CO_3^{\bullet -}]_t} = k_2{}'t \qquad (24)$$

As found in this work, the equilibrium constant K_2 is large and the $CO_3^{\bullet -}$ can be immediately converted to $(CO_3)_2^{\bullet 3-}$. Therefore, eqs 23 and 24 are principally identical and the previously reported k_2 values remain valid. By replacing the $(CO_3)_2^{\bullet 3-}$ concentration with the optical absorption at a certain wavelength, k_2 can be experimentally determined.

The rate constant k_1 for the reaction of $OH^{\bullet}$ with HCO_3^- in $NaHCO_3$ solution can be similarly derived. However, due to the smaller equilibrium constant (K_1) for $H(CO_3)_2^{\bullet 2-}$ than that for $(CO_3)_2^{\bullet 3-}$, a fitting of the absorption buildup due to the carbonate radical by the formula similar to eq 23 may not precisely provide a straight line and the obtained rate constant is probably somewhat underestimated. Of course, the hydrolysis of the carbonate and bicarbonate ions should be corrected.

Conclusions

The absorption spectrum of the carbonate radical was found to be nearly invariant from 25 to 400 °C, indicating that the carbonate radical is very stable. The temperature dependence of the absorbance of the carbonate radical was investigated over a wide temperature range in $NaHCO_3$ and Na_2CO_3 solutions. There is a clear difference in temperature dependence of the absorbance between $NaHCO_3$ and Na_2CO_3 solutions. To explain this, we proposed that the carbonate radical is a dimer radical anion, in the form of either $(CO_3)_2^{\bullet 3-}$ or $H(CO_3)_2^{\bullet 2-}$, depending on pH of the solution. Their equilibrium constants were obtained for temperatures of 25−250 °C. The concentration dependence of the absorbance observed at various temperatures can correlate well with the simulation results from the dimer model. Moreover, using the equilibrium constants K_1 and K_2, the pK_a values of $H(CO_3)_2^{\bullet 2-}$ at various temperatures were calculated. The pK_a at 25 °C was 9.30 ± 0.15, in good agreement the literature values of 9.5−9.6.

The temperature dependence of the decay was also investigated. There is a small difference between $NaHCO_3$ and Na_2CO_3 solutions below 200 °C and almost no difference was identified at temperatures above 200 °C. This is due to the fact that most of the CO_3^{2-} ions will be hydrolyzed to HCO_3^- ions if the initial concentration of Na_2CO_3 is not high. The insignificant temperature dependence of the decay over 25−300 °C is explained by the acid−base equilibrium of the carbonate radical.

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