Carbonate Radical Formation in Radiolysis of Sodium Carbonate and Bicarbonate Solutions up to 250 °C and the Mechanism of its Second Order Decay

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Carbonate Radical Formation in Radiolysis of Sodium Carbonate and Bicarbonate Solutions up to 250 °C and the Mechanism of its Second Order Decay

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Pulse radiolysis experiments published several years ago (*J. Phys. Chem. A*, **2002**, *106*, 2430) raised the possibility that the carbonate radical formed from reaction of ·OH radicals with either HCO_3^- or CO_3^{2-} might actually exist predominantly as a dimer form, for example, $\cdot(CO_3)_2^{3-}$. In this work we re-examine the data upon which this suggestion was based and find that the original data analysis is flawed. A major omission of the original analysis is the recombination reaction $\cdot OH + \cdot CO_3^- \rightarrow HOOCO_2^-$. Upon reanalysis of the published data for sodium bicarbonate solutions and analysis of new transient absorption data we are able to establish the rate constant for this reaction up to 250 °C. The mechanism for the second-order self-recombination of the carbonate radical has never been convincingly demonstrated. From a combination of literature data and new transient absorption experiments in the 1−400 ms regime, we are able to show that the mechanism involves pre-equilibrium formation of a $C_2O_6^{2-}$ dimer, which dissociates to CO_2 and peroxymonocarbonate anion:

$$\cdot CO_3^- + \cdot CO_3^- \leftrightarrow C_2O_6^{2-} \rightarrow CO_2 + O_2COO^{2-}$$

$\cdot CO_3^-$ reacts with the product peroxymonocarbonate anion, producing a peroxymonocarbonate radical $\cdot O_2COO^-$, which can also recombine with the carbonate radical:

$$\cdot CO_3^- + CO_4^{2-} \rightarrow \cdot CO_4^- + CO_3^{2-}$$

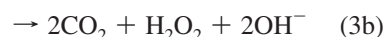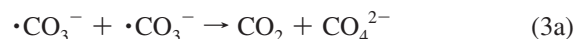$$\cdot CO_3^- + \cdot CO_4^- \rightarrow C_2O_7^{2-}$$
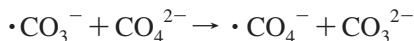
I. Introduction

The carbonate anion radical $\cdot CO_3^-$ is one of the most extensively studied inorganic radicals due to its ubiquitous nature in the environment, its relatively long lifetime, and its accessible absorption at 600 nm.[1−15] Typically the species is generated by $\cdot OH$ radical reaction with either CO_3^{2-} or HCO_3^- ion as in reactions 1 and 2:

$$\cdot OH + CO_3^{2-} \rightarrow \cdot CO_3^- + OH^- \qquad (1)$$

$$\cdot OH + HCO_3^- \rightarrow \cdot CO_3^- + H_2O \qquad (2)$$
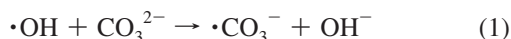
Since direct measurement of the weak UV absorption of $\cdot OH$ is difficult, the carbonate ion is particularly useful as a scavenger for $\cdot OH$ radicals in laboratory studies. A study of the carbonate radical yield in pulse radiolysis of both carbonate and bicarbonate solutions at elevated temperature[15] suggested several years ago that the radical actually exists in a dimeric form, for example, $\cdot(CO_3)_2^{3-}$. In this work we re-examine the evidence cited for this claim and show it to be based on a flawed analysis. However, we also confirm

the observation[15] that decay of the radical deviates significantly from simple second-order kinetics when the radical is generated in bicarbonate solutions. We review the evidence available for the recombination reaction and suggest a mechanism that can explain the data.

For such a well-known radical, the structure, acid/base properties, and recombination mechanism of $\cdot CO_3^-$ have remained controversial for a very long time. The first comprehensive study of the carbonate radical using pulse radiolysis was accomplished by Weeks and Rabani,[1] who recorded the transient spectrum and investigated the decay kinetics as a function of pH. They found the decay of the carbonate radical in alkaline solution was second order over 80% of the decay, but deviated from second-order kinetics at longer time. A shift in the nature of the deviation could be seen between pH 11.5 and 13. The authors provided no explanation for the deviation from second order. Two sets of reaction products were postulated as consistent with the data:

$$\cdot CO_3^- + \cdot CO_3^- \rightarrow CO_2 + CO_4^{2-} \qquad (3a)$$

$$\rightarrow 2CO_2 + H_2O_2 + 2OH^- \qquad (3b)$$

Behar et al. generated the carbonate radical in oxygenated solutions both by radiolysis and by photolysis of hydrogen

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peroxide solutions.[2] They measured the reaction rates of carbonate radical with both H_2O_2 and HO_2^-, finding a much faster rate for HO_2^-:

$$\cdot CO_3^- + H_2O_2 \rightarrow \cdot HO_2 + HCO_3^- \qquad (4)$$

$$\cdot CO_3^- + HO_2^- \rightarrow \cdot O_2^- + HCO_3^- \qquad (5)$$
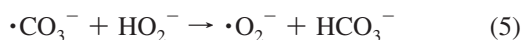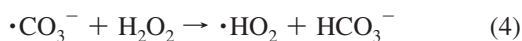
They explained the deviation from second-order kinetics observed by Weeks and Rabani[1] as the reaction of carbonate radical with the peroxide generated as a product of the recombination, according to reaction 3b. The pH dependence around pH = 12 results from the acid–base equilibrium of H_2O_2 and HO_2^-, and the very different rates of reactions 4 and 5.[2] Behar et al. discounted the possibility that the carbonate radical itself might be present in an acid–base equilibrium 6 in the pH range studied:

$$\cdot HCO_3^- \leftrightarrow H^+ + \cdot CO_3^- \qquad (6)$$

Lilie et al.[4] applied simultaneous transient absorption and conductivity detection to the study of $\cdot CO_3^-$ reactions. On the basis of the conductivity transients, these authors ruled out the second-order recombination mechanism 3b in favor of 3a. They provided no explanation for the pH-dependent deviation from second-order kinetics seen by other workers.
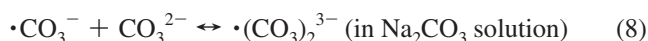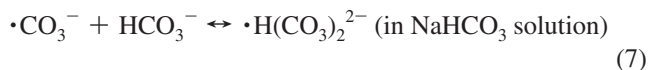
Chen, Cope, and Hoffman[3] also found pH-dependent deviation from second-order decay kinetics in alkaline solution. From kinetic measurements in the presence of added solutes the authors concluded that the pK_a of $\cdot HCO_3$ in reaction 6 is 9.6 ± 0.3. However, their measured rate constants of recombination at high pH were systematically higher than those reported in other studies.

Eriksen et al. used the $\cdot CO_3^-$ radical as a one-electron oxidant in studies of cyclic hydrazines in the pH region reported by Chen et al.,[3] but found no indication of a possible protonation of the $\cdot CO_3^-$ radical.[5,6] In further investigations[16] they reported a range of 7.0–8.2 for the pK_a based on an increase in the initial absorbance of the radical with pH. This study also first reported a negative temperature coefficient for the recombination reaction 3, although no data was presented. It was proposed that the reaction involves a pre-equilibrium with the short-lived intermediate $C_2O_6^{2-}$. The negative temperature coefficient was later confirmed by Ferry and Fox[12] who found the rate constant increases again dramatically above 300 °C.

Bisby, et al.[10] investigated the structure of the carbonate radical using time-resolved resonance Raman spectroscopy. They found no change of the radical's Raman spectrum between pH 7.5 and 13.5, and concluded that the pK_a for reaction 6 must be less than 7.5. Using a stop-flow/pulse radiolysis technique, Czapski et al.[11] made measurements of the (relatively slow) reaction of $\cdot OH$ radical with carbonic acid in acidic solution. They found the same spectrum of carbonate radical with 600 nm maximum that is found in neutral and alkaline solutions and concluded that the radical $\cdot HCO_3$ is a strong acid with pK_a < 0. At roughly the same time, Zuo et al.[13] investigated the pH dependence of reactivity of the (bi)carbonate radical in mixed carbonate/SCN solutions and concluded the $\cdot HCO_3$ radical must have a pK_a of 9.6. Lymar, Schwarz, and Czapski[14] published a rebuttal of the pK_a claims made in Zuo et al.,[13] Chen et al.,[3] and Eriksen et al.,[16] showing how each of these studies had

reached an incorrect conclusion, and reiterated their earlier conclusion that pK_a for reaction 6 is less than 0.

It would seem that the work of Lymar et al.[14] and the Raman study of Bisby et al.[10] had settled the issue of $\cdot CO_3^-$ radical structure and pK_a. However, the U. Tokyo group[15] then published a survey of carbonate radical yield and second-order decay in a wide concentration range of carbonate and bicarbonate solutions up to 350 °C. To explain apparent anomalies in the yield and decay, Wu et al.[15] proposed that the carbonate radical is normally present in the form of a dimer anion, either $\cdot (CO_3)_2^{3-}$ or $\cdot H(CO_3)_2^{2-}$ formed via the following reaction processes:

$$\cdot CO_3^- + HCO_3^- \leftrightarrow \cdot H(CO_3)_2^{2-} \text{ (in NaHCO}_3 \text{ solution)} \qquad (7)$$

$$\cdot CO_3^- + CO_3^{2-} \leftrightarrow \cdot (CO_3)_2^{3-} \text{ (in Na}_2CO_3 \text{ solution)} \qquad (8)$$

which are converted between the acid and base forms via:

$$\cdot H(CO_3)_2^{\cdot 2-} \leftrightarrow H^+ + \cdot (CO_3)_2^{\cdot 3-} \qquad (9)$$
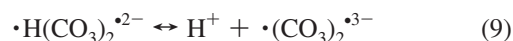
Using this model and equilibrium constants determined from their data, Wu et al.[15] calculated the pK_a of the dimer in reaction 9 to be 9.30 ± 0.15. The authors speculate that the pK_a of 9.5–9.6 previously determined for the assumed $\cdot HCO_3$ at room temperature is actually the value for $\cdot H(CO_3)_2^{2-}$ and that the dimer model is quite reasonable by analogy with other radicals having the $\cdot X_2^-$ formula.

Upon considering the Tokyo group's evidence and kinetic model, we found two serious flaws. The first of these is the omission, in considering the acid–base equilibria of the carbonate/bicarbonate/carbonic acid system, of the additional equilibrium 12 to form aqueous CO_2 from carbonic acid:

$$HCO_3^- \leftrightarrow H^+ + CO_3^{2-} \qquad (10)$$

$$H_2CO_3 \leftrightarrow H^+ + HCO_3^- \qquad (11)$$

$$H_2CO_3 \leftrightarrow CO_2 + H_2O \qquad (12)$$

At elevated temperature this is a serious flaw: at 250 °C, less than half of the expected scavenger concentration is actually present in the form of bicarbonate ion (see below). Second, for low concentrations of the bicarbonate or carbonate scavenger for $\cdot OH$ radicals, the $\cdot OH$ radical persists for a relatively long time in the presence of $\cdot CO_3^-$ radicals. In this situation the cross-recombination of $\cdot CO_3^-$ radicals with $\cdot OH$ cannot be ignored as it was by Wu et al.[15]

In the following sections we describe and evaluate a kinetic model using the ideas laid out in the last paragraph and fit the Tokyo group's data to estimate the $\cdot CO_3^- + \cdot OH$ reaction rate. We use the model to fit pulse radiolysis/transient absorption experiments and explain carbonate radical yields, without the need to postulate a dimer radical form. Then, we consider the curious observations of second-order decay rate constant of the carbonate radical in $NaHCO_3$ and Na_2CO_3 solutions. The mechanism for the second order recombination has never been fully and convincingly worked out. We propose a mechanism that is fully consistent with the data.

II. Experimental Section

Experiments Performed at Argonne National Laboratory. Pulse radiolysis/transient absorption experiments were carried out using 4−40 ns pulses from the Argonne Chemistry Division's 20-MeV electron linac, where longer pulse width corresponds to higher applied dose. The differing pulse widths used have negligible impact on the observed kinetics, which occur on a time scale of several microseconds. The high-temperature/pressure sample cell, flow system, and basic experimental setup and characteristics were described in previous publications.[17−24] Normal temperature and pressure stabilities were ±0.2 °C and ±0.1 bar, respectively. Analyzing light from a pulsed 75 W xenon lamp (Photon Technology International) was selected using a 40 nm bandwidth interference filter (Andover Corporation) centered at 600 nm, the wavelength corresponding to the maximum absorption of $\cdot CO_3^-$ (ϵ_{max} at 600 nm = 1970 M^{-1} cm^{-1}).[14] The same filter was used for all data collection, as the maximum absorption is known not to shift with temperature changes.[15] A silicon photodiode (FFD-100, EG&G) was used for detection. Kinetics were measured at 100, 200, 225, and 250 °C.

Sodium bicarbonate ($NaHCO_3$) solutions were prepared at a concentration of 0.0200 M (sodium hydrogen carbonate, Aldrich, 99.99% + used as received) in deionized water (18.2 MΩ-cm, Barnstead Nanopure cartridge system). Water was degassed with dry nitrogen gas for ∼30 min prior to adding sodium bicarbonate to avoid contamination by carbonate ions arising from possible carbon dioxide absorption. For experiments, the $NaHCO_3$ concentration was controlled by mixing with a separate deionized water sample using two separate HPLC pumps (Alltech 301). The water sample was also previously degassed with nitrogen. Immediately before performing kinetic experiments, both the $NaHCO_3$ solution and deionized water samples were purged with N_2O gas for ∼30 min, giving an N_2O concentration of 0.024 m. Samples were then kept under an N_2O atmosphere throughout experiments.

Two or three concentrations of $NaHCO_3$ were used at each temperature, as diluted by mixing with deionized water. At 100 °C, concentrations were 0.00188, 0.00313, and 0.00625 m (molal); at 200 °C, concentrations were 0.00177, 0.00313, and 0.00625 m; and at 225 and 250 °C, concentrations were 0.00313 and 0.00625 m. Total system flow rate was 1.6 mL/min, and the experimental pressure was 250 bar. Multiple doses from the linac were used at each temperature in order to extract rate information due to influence of the second-order chemistry. Four to six doses were applied at each temperature, producing final $\cdot CO_3^-$ concentrations between ∼ 0.7 and 5 × 10^{-6} m.

Experiments Performed at Notre Dame Radiation Laboratory. Pulse radiolysis/transient absorption experiments were carried out using 4−50 ns pulses from the Notre Dame Radiation Laboratory's 8 MeV electron linac, where longer pulse width corresponds to higher applied dose. An OLIS RSM-2000 time-resolved spectrometer was used to record the kinetics, with dual beam fixed wavelength detection at 600 nm.

Sodium bicarbonate ($NaHCO_3$) solutions were prepared at a concentration of 0.0400 M (sodium hydrogen carbonate, Aldrich, 99.998% + used as received) in purified deionized water (resistivity 18 MΩ-cm, total organic carbon <5 ppb as CO_2, Serv-A-Pure Co. cartridge system.)

Sodium carbonate (Na_2CO_3) solutions were prepared at a concentration of 0.0400 M (sodium carbonate, Aldrich, 99.98% + used as received.)
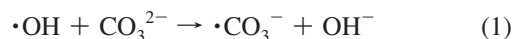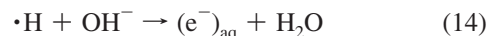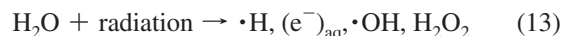
Water was sparged with N_2O gas for ca. 30 min prior to adding sodium bicarbonate or sodium carbonate to avoid bubbling out CO_2. Final concentrations were generated by diluting the stock with N_2O-bubbled deionized water. A 1 cm^3 portion of solution was then measured into a disposable UV-grade plastic (methyl methacrylate) cuvette and sealed with a Parafilm cover. The sample was very briefly sparged with N_2O again using syringe needles inserted into the sample. Care was taken not to change the carbonate or bicarbonate concentration and pH by bubbling out CO_2. The sample volume was carefully limited to 1 cm^3 in order to be certain the entire solution obtained a uniform dose from the electron beam: on time scales of hundreds of milliseconds and longer, convection can be expected to relax any concentration gradients produced, which would distort kinetic analysis.

Each sample was typically irradiated with five linac pulses with a transient absorption recorded for each. The first four were intended to record the kinetic decay out to baseline at roughly one-half of a second. It was possible to observe the buildup of reactive product (e.g., hydrogen peroxide) as the decay became shorter on each pulse. On the fifth pulse the time base was set to the maximum 1 μs/point resolution in order to more precisely set the initial amplitude and time zero for kinetic analysis. A fresh cuvette was used for each sample set. The empty cuvettes displayed no transient absorption or fluorescence.

III. Results and Discussion

Formation Rate and Yield of the Carbonate Radical. In N_2O-saturated solutions of carbonate and bicarbonate ions, the carbonate radical is formed by water radiolysis in the following sequence of reactions:

$$H_2O + radiation \rightarrow \cdot H, (e^-)_{aq}, \cdot OH, H_2O_2 \quad (13)$$

$$\cdot H + OH^- \rightarrow (e^-)_{aq} + H_2O \quad (14)$$

$$(e^-)_{aq} + N_2O \rightarrow N_2 + OH^- + \cdot OH \quad (15)$$

$$\cdot OH + CO_3^{2-} \rightarrow \cdot CO_3^- + OH^- \quad (1)$$

$$\cdot OH + HCO_3^- \rightarrow \cdot CO_3^- + H_2O \quad (2)$$

Assuming a sufficient concentration of carbonate or bicarbonate scavenger, all of the radicals initially formed by radiolysis can be converted to $\cdot CO_3^-$, and this method has been used to estimate the total radiolysis yield up to high temperature (in alkaline solution).[25] Buxton, et al.[7] measured the rise of the $\cdot CO_3^-$ radical absorbance in carbonate/bicarbonate solutions up to 250 °C. They deduced that reactions 1 and 2 have nearly identical Arrhenius activation energy, but reaction 2 has 50 times smaller pre-exponential factor than reaction 1. Their analysis strongly relied on the temperature-dependent acid−base equilibrium constants for the bicarbonate ion:

$$HCO_3^- \leftrightarrow H^+ + CO_3^{2-} \quad (10)$$

The equilibrium in their experiment was controlled by the addition of NaOH.

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TABLE 1: Percentage of Bicarbonate Remaining in Solution

T (°C)	% of bicarbonate remaining			
	0.001 M	0.002 M	0.02 M	0.1 M
0	98.6	98.6	98.6	98.6
25	97.1	97.1	97.1	97.1
50	96.5	96.6	96.6	96.6
75	95.3	95.7	95.9	95.9
100	93.3	94.2	94.8	94.8
125	90.1	91.8	93.2	93.3
150	85.5	88.1	90.8	90.8
175	79.1	82.9	86.9	87.0
200	70.5	75.4	80.7	80.9
225	59.3	65.0	70.7	70.9
250	45.5	50.9	55.7	55.8

In "natural pH" solutions of carbonate or bicarbonate ions at elevated temperature, the equilibrium strongly shifts away from carbonate ion toward bicarbonate and carbonic acid. In fact, the equilibrium shifts even further toward the CO_2 product of reaction 12.

$$H_2CO_3 \leftrightarrow H^+ + HCO_3^- \tag{11}$$

$$H_2CO_3 \leftrightarrow CO_2 + H_2O \tag{12}$$

Table 1 indicates, for natural pH solutions of sodium bicarbonate of various concentrations, the fraction that actually remains in the form of bicarbonate ion. At 250 °C, roughly 50% of the bicarbonate has converted to dissolved CO_2 and carbonic acid. As demonstrated by Czapski et al.,[11] the reaction rate of $\cdot OH$ radical with H_2CO_3 is 75 times smaller than reaction 2 at room temperature and can probably be ignored.

Wu et al.[15] published an extensive survey of the yield of carbonate radical versus temperature in a series of natural pH carbonate and bicarbonate solutions of widely varying concentration (0.1–0.001 m). Their data for the initial absorbance of bicarbonate solutions is replotted in Figures 1 and 2, for samples irradiated with 30 Gy/pulse, and assuming extinction coefficient 1700 M^{-1} cm^{-1} at 633 nm independent of temperature. It is very clear that as concentration of bicarbonate is lowered from
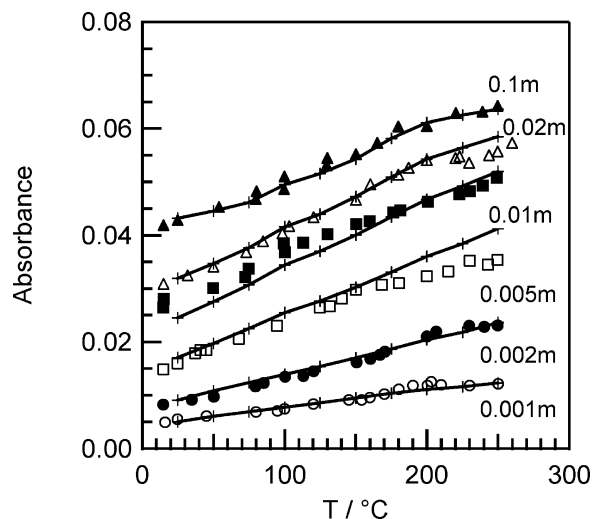

Figure 1. Absorbance of the carbonate radical in $NaHCO_3$ at 633 nm vs temperature. The markers represent data of Wu et al.,[15] and the lines represent simulations, as described in this work.
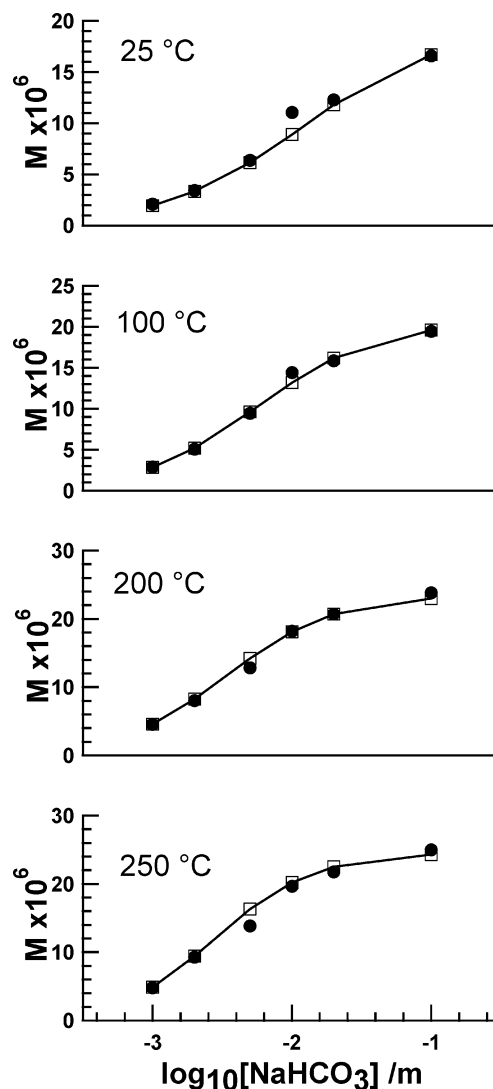

Figure 2. Comparison of the simulated and measured yields for the carbonate radical in $NaHCO_3$. ● Wu, et al.[15] experiment; □ kinetic model, this work.

0.1 m, the yield of $\cdot CO_3^-$ radicals decreases, that is, scavenging of the $\cdot OH$ radicals is incomplete. A similar but more complicated figure was published for the case of CO_3^{2-} solutions, where due to the higher scavenging rate of reaction 1, incomplete scavenging occurs at lower solute concentrations.[15] In this situation of incomplete scavenging of $\cdot OH$, a quantitative description of the formation kinetics requires the following additional reactions:

$$\cdot OH + \cdot OH \rightarrow H_2O_2 \tag{16}$$

$$\cdot OH + \cdot CO_3^- \rightarrow HOOCO_2^- \tag{17}$$

$$\cdot H + \cdot OH \rightarrow H_2O \tag{18}$$

$$\cdot H + \cdot CO_3^- \rightarrow HCO_3^- \tag{19}$$

Wu et al.[15] simulated their experimental results in both carbonate and bicarbonate solutions from 25 to 250 °C but reported they were only able to obtain quantitative agreement at the highest concentration, that is, in the limit of complete scavenging. To better explain their results, Wu et al. postulated that the carbonate radical actually exists as a dimer, that is,

TABLE 2: Kinetic Parameters of Carbonate Radical Growth and Decay

solution	$[HCO_3^-]$	$[CO_3^{2-}]$	pH	ionic strength	k_3 (±10%)	$k_4 + k_5$ (±50%)	$k_{22} + k_{23}$ (±50%)
bicarbonate							
0.10 M	0.097	1.50×10^{-3}	8.4	0.10 M	7.5×10^6	8×10^5	3.0×10^5
0.04 M	0.0388	5.99×10^{-4}	8.4	0.04 M	6.3×10^6	8×10^5	3.0×10^5
0.02 M	0.0194	2.99×10^{-4}	8.4	0.02 M	5.7×10^6	8×10^5	3.0×10^5
carbonate							
0.0050 M	0.94×10^{-3}	4.06×10^{-3}	11.0	0.014 M	5.4×10^6	3.5×10^6	2.0×10^6
0.0025 M	0.64×10^{-3}	1.86×10^{-3}	10.8	6.85×10^{-3} M	5.1×10^6	2.0×10^6	1.4×10^6
0.0010 M	0.63×10^{-3}	0.37×10^{-3}	10.6	2.63×10^{-3} M	4.8×10^6	1.3×10^6	1.3×10^6

	reaction	rate constant ($M^{-1} s^{-1}$)	source
Carbonate Growth Kinetics			
1	$\cdot OH + CO_3^- \rightarrow \cdot CO_3^- + OH^-$	4.0×10^8	ref 7
2	$\cdot OH + HCO_3^- \rightarrow \cdot CO_3^- + H_2O$	1.0×10^7	ref 7
14	$\cdot H + OH^- \rightarrow (e^-)_{aq} + H_2O$	2.5×10^7	ref 28
15	$(e^-)_{aq} + N_2O \rightarrow N_2 + OH^- + \cdot OH$	9.0×10^9	ref 38
16	$\cdot OH + \cdot OH \rightarrow H_2O_2$	4.3×10^9	ref 29
17	$\cdot OH + \cdot CO_3^- \rightarrow HOOCO_2.$	$6.5 \pm 1.5 \times 10^9$	fitting, this work
18	$\cdot H + \cdot OH \rightarrow H_2O$	9.7×10^9	ref 26
19	$\cdot H + \cdot CO_3^- \rightarrow HCO_3^-$	2.5×10^9	estimate, this work
Carbonate Decay Kinetics			
3	$\cdot CO_3^- + \cdot CO_3^- \rightarrow CO_2 + CO_4^{2-}$	$k_0 = 4.25 \pm 0.4 \times 10^6$	fitting, this work
4	$\cdot CO_3^- + H_2O_2 \rightarrow \cdot HO_2 + HCO_3^-$	8×10^5	ref 2
5	$\cdot CO_3^- + HO_2^- \rightarrow \cdot O_2^- + HCO_3^-$	above	fitting, this work
20	$\cdot CO_3^- + \cdot O_2^- \rightarrow CO_5^{2-}$	$k_0 = 2.0 \pm 0.2 \times 10^8$	fitting, this work
22	$\cdot CO_3^- + HCO_4^- \rightarrow HCO_3^- + \cdot CO_4^-$	above	fitting, this work
23	$\cdot CO_3^- + CO_4^{2-} \rightarrow CO_3^{2-} + \cdot CO_4^-$	above	fitting, this work
24	$\cdot CO_3^- + \cdot CO_4^- \rightarrow C_2O_7^{2-}$	$k_0 = 1.0 \times 10^9$	estimate, this work

$\cdot CO_3^-$ reacts with the parent compound to give $\cdot(CO_3)_2^{3-}$ and/or $\cdot H(CO_3)_2^{2-}$. The pK_a around 9.5 attributed to $\cdot HCO_3$ radical in other studies would then correspond to the dimer radical, and the yield behavior illustrated in Figures 1 and 2 can be approximately explained in terms of the dimerization equilibria and the difference in absorbance of the dimer and monomer forms.

Objections to this proposal have already been mentioned in the introduction. The apparent pK_a at 9.5 was already shown to be an experimental artifact.[14] Resonance Raman data shows that the absorbing radical species has C_{2v} symmetry regardless of pH, with no proton frequency apparent.[10] The most compelling objection is that the data can be explained with a more complete mechanism. Although Wu et al.[15] made use of the carbonate/bicarbonate/carbonic acid equilibria 10 and 11, they failed to include equilibrium 12 between CO_2 and carbonic acid. Table 1 demonstrates the importance of this equilibrium. (Solution of the coupled equilibrium equations is given in the Supporting Information.) Of greater importance still, they failed to include in their (monomer) simulation the radical recombination reaction 17 between $\cdot OH$ radical and $\cdot CO_3^-$. As we now show, the data of Wu et al. can be fit to extract this rate constant as a function of temperature.

The carbonate radical absorbance at 633 nm versus temperature for irradiation of sodium bicarbonate solutions was extracted from Figure 5a presented by Wu et al.[15] and was replotted and then smoothed with a third-degree polynomial in order to obtain the absorbance at 25 °C intervals. These numbers are plotted in Figure 1. For bicarbonate concentrations of 0.001, 0.002, 0.005, 0.01, 0.02, and 0.1 m,

a system of kinetic equations corresponding to reactions 1, 2, and 13−19 was integrated for the temperature range up to 250 °C. (A summary list of the reactions can be found in Table 2.) Integration was performed with a fifth-order Runge−Kutta algorithm with adaptive step size in the IGOR software package of Wavemetrics, Inc. Yields of the free radicals vs temperature in eq 13 were taken from Elliot.[26] Reaction 14 was taken from Marin et al.[27] and Han et al.[28] The rate constants for scavenging of the OH radical, reactions 1 and 2, were taken from Buxton et al.[7] Reaction 16 rate constants were published recently by Janik et al.[29]

Reactions 18 and 19 determine the fate of the $\cdot H$ atom, which is the primary uncertainty of the mechanism (plus or minus 10% of the yield) in N_2O-saturated bicarbonate solutions. The temperature-dependent rate constants for reaction 18 were taken from the review of Elliot.[26] For lack of any data, the same numbers were used for reaction 19, which we assume will occur with similar rate constant. The effect of the two reactions is to reduce the yield of $\cdot CO_3^-$ by the yield of $\cdot H$ atoms. In high temperature alkaline solutions, reaction 14 may convert $\cdot H$ atoms to $(e^-)_{aq}$ before reactions 18 or 19 occur. In this limit, the yield of $\cdot CO_3^-$ may be augmented by the yield of $\cdot H$ atoms.

The experimental $\cdot CO_3^-$ radical yields of ref 15 cannot be fit when reaction 17 is not included. The self-recombination rate of $\cdot OH$ radicals provides insufficient competition to produce the low radical yields observed. We found a best value for the reaction 17 rate constant by slightly adjusting the dose to agree with the highest bicarbonate concentration and then adjusting the rate of reaction 17 to agree with the
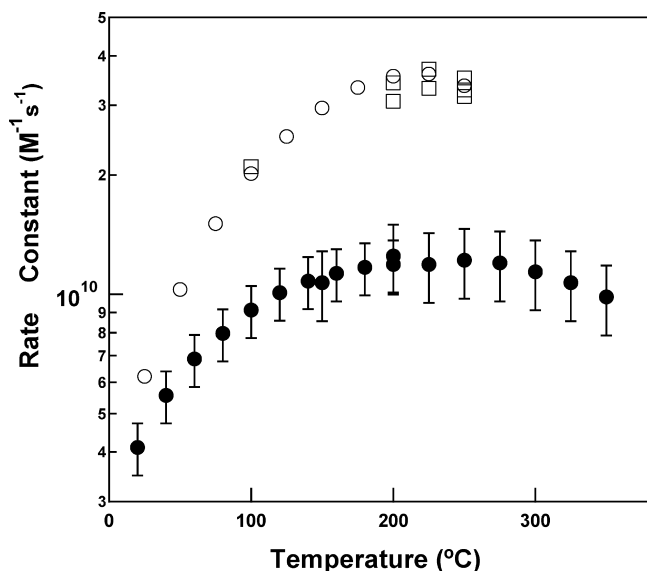
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Figure 3. Temperature dependence of second-order OH recombination reaction rates. ●, ·OH + ·OH; ○, ·CO$_3^-$ + ·OH from refit of Wu et al.[15] data; □, ·CO$_3^-$ + ·OH from this work.

lowest bicarbonate concentration at each temperature. The "fit" to the data of Wu et al.[15] is superimposed on the data in Figure 1. The same comparison is illustrated for four temperatures in Figure 2 in the format used by Wu et al. to demonstrate their dimer model. Agreement between the data and our simulation appears somewhat better than for the dimer proposal.

The rate parameters deduced for reaction 17 up to 250 °C are plotted in Figure 3 in comparison with the rate constant for recombination of OH radicals. Both rate constants appear to approach a limiting value above 200 °C. To confirm the accuracy of the rate constants for reaction 17 we carried out fits of unpublished scavenging data collected some years ago at Argonne National Laboratory. Data for two different N$_2$O-saturated samples of sodium bicarbonate are shown in Figure 4. Transient absorption was recorded at 600 nm for a series of different electron pulse widths to vary the dose. The traces are fit globally with common rate constants, using the same chemical model described above, and extinction coefficient of 2000 M^{-1} cm^{-1}. The resulting values for reaction 17 are shown

by the open squares in Figure 3. Agreement with our analysis of the data from Wu et al.[15] is excellent.

For the ·OH + ·OH recombination 16, the high temperature limiting behavior is understood as the high pressure limit for the gas phase reaction.[29] Water essentially acts as a very efficient third body to ensure the radical pair is always in thermal equilibrium with the surroundings. The barrier to reaction is entropic or steric—i.e., the proper orientation must be achieved in a collision to find the energetically downhill channel. At lower temperatures, diffusion is slower and the solvent caging phenomenon provides enough recollisions that the proper orientation is usually found in a single diffusional encounter. In this regime (e.g., near room temperature) the rate constant approaches the diffusion limit. At higher temperatures too few recollisions occur before the radicals diffuse apart again. We propose that the same "steric effect" explanation might account for the high temperature limiting behavior of rate constant 17, as in both cases a peroxide bond is being formed and a particular orientation must be achieved for reaction.

The excellent agreement of our model based on reactions 1, 2, and 13−19 with the experimental data appears to settle the issue of ·CO$_3^-$ yield versus scavenger concentration and temperature raised in ref 15. The title of ref 15 asks the rhetorical question "Is the radical a single anion?" We feel we can definitively answer "yes."

Decay of the Carbonate Radical. Although the analysis and experiments detailed in the previous sections seem to settle the issue of temperature dependence of the ·CO$_3^-$ radical radiolysis yields, there remains the issue of concentration-dependence of the second-order decay in carbonate or bicarbonate solutions. Wu et al.[15] find that the apparent rate constant for second-order decay, measured in the first 5 ms, becomes faster in bicarbonate solutions with concentration below 0.02 m at all temperatures. In carbonate solutions they reported a similar behavior only at temperatures above 100 °C. Their explanation for this phenomenon involves the properties of the postulated dimeric form of carbonate radical, which we have concluded is not present.

A proper understanding of the phenomenon should begin with consideration of the second-order decay mechanism. We are surprised to find that there has been no definitive exposition of the mechanism for this reaction. A starting point is to consider the relatively low observed rate constant, with $2k = 1 \times 10^7$
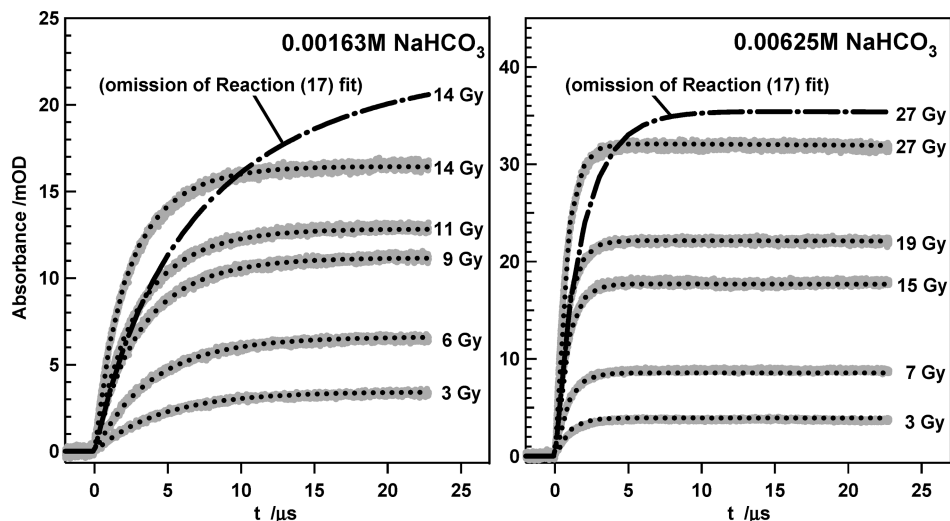

Figure 4. Fit of rise of 600 nm ·CO$_3^-$ absorbance in (a) 0.00163 M NaHCO$_3$ and (b) 0.00625 M NaHCO$_3$ solutions at 200 °C. Experimental data, ···; simulation curve, ---; −·−·− represents fits similar to those suggested by Wu et al.,[15] omitting reaction 17, ·OH + ·CO$_3^-$ → HOOCO$_2^-$.

$M^{-1} s^{-1}$, some 2 orders of magnitude below the diffusion limit. Rate constants for the second-order decay up to supercritical temperature have been reported by Ferry and Fox[12] and by Wu et al.[15] for carbonate solutions. Both groups report a slight negative temperature coefficient up to 300 °C and then a sharp increase at higher temperature. This is most readily explained by the presence of a short-lived intermediate peroxydicarbonate $C_2O_6^{2-}$ species and a pre-equilibrium as first suggested by Eriksen, et al.:[16]

$$\cdot CO_3^- + \cdot CO_3^- \leftrightarrow C_2O_6^{2-} \rightarrow products \qquad (3d)$$
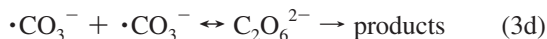
We investigated the properties of the $C_2O_6^{2-}$ dimer intermediate via ab initio calculations using the Gaussian 03 program package.[30] Details are set forth in the Supporting Information. Using aug-cc-pvDZ basis set, at MP2 or B3LYP theory level, a peroxy link is formed, with O−O distance of 1.48 Å. The C−O−O angles are 112°, but the C−O−O−C tortion is nearly free to rotate with a very shallow minium near 130°. At the QCISD level of theory, free energy of the reaction 3d to form the gas phase dimer is +297 kJ/mol. Solvation of both reactants and dimer product in "water" using the polarized continuum model of Tomasi, et al.[31] favors the dimer by 297 kJ/mol at MP2 level, and by 304 kJ/mol in a B3LYP density functional calculation. Assuming a similar solvent stabilization at the QCISD or higher theory level, it appears the dimer formation from two carbonate radicals should be roughly thermoneutral in water, consistent with the postulated pre-equilibrium.

Weeks and Rabani[1] postulated two possible sets of products for reaction 3:

$$\cdot CO_3^- + \cdot CO_3^- \rightarrow CO_2 + CO_4^{2-} \qquad (3a)$$

$$\rightarrow 2CO_2 + H_2O_2 + 2OH^- \qquad (3b)$$

Deviation of the decay kinetics from pure second order (for pH below 11.5) was observed by Weeks and Rabani[1] and subsequently explained by Behar et al.[2] in terms of H_2O_2 product. According to these authors, at later stages of the $\cdot CO_3^-$ decay, as H_2O_2 product has built up, reaction 4 becomes dominant,

$$\cdot CO_3^- + H_2O_2 \rightarrow HCO_3^- + \cdot O_2^- + H^+ \qquad (4)$$
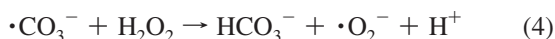
and the decay is autocatalytic. Production of the superoxide anion product in reaction 4 means reaction 20 should also be considered as part of the decay.
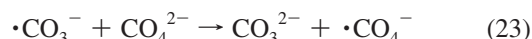
$$\cdot CO_3^- + \cdot O_2^- \rightarrow CO_5^{2-} \qquad (20a)$$

$$CO_5^{2-} \rightarrow CO_3^{2-} + O_2 \qquad (20b)$$
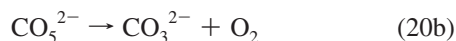
Reaction 20a was shown by Behar, et al.[2] to be quite fast (4 × 10^8 $M^{-1} s^{-1}$ at 3 M ionic strength), so it effectively doubles the effect of reaction 4 or 5. The CO_5^{2-} product persists for several seconds before it dissociates to carbonate ion and O_2.

Mechanism 3b suggested by Weeks and Rabani[1] seems to be preferred on the basis of hydrogen peroxide product, to explain the observed deviation of kinetics from second order. However, in simultaneous optical/conductivity experiments of Lilie et al.,[4] it was found that after an initial conductivity jump at the radiolysis pulse (from net production of OH^- in reaction 1) there is virtually no conductivity change during the second-order decay of the carbonate radicals. Subsequent slow decay of the conductivity back to baseline is consistent with saponification of CO_2, and demonstrates that one and only one CO_2 molecule is produced in each bimolecular recombination reaction. These authors definitively ruled out mechanism 3b in favor of 3a.

If 3b is ruled out, then the autocatalytic nature of the decay must stem from a reaction of $\cdot CO_3^-$ with the peroxymonocarbonate anion. Within the past decade peroxymonocarbonate has been recognized as an important oxidant in biological systems[32,33] thanks to the equilibrium 21 of bicarbonate and hydrogen peroxide

$$HCO_3^- + H_2O_2 \leftrightarrow HCO_4^- + H_2O \qquad (21)$$

The pK_a of HCO_4^- is estimated as 10.6, similar to bicarbonate anion.[34] Equilibrium constant k_{21} has been measured by carbon 13 NMR to be 0.32 M^{-1} at room temperature.[35] The hydrolysis (reverse) reaction giving bicarbonate and hydrogen peroxide has rate constant $k_{21r} = 1.2 \times 10^{-3} s^{-1}$. Under the experimental conditions of most pulse radiolysis experiments, the decay of peroxymonocarbonate into H_2O_2 and bicarbonate is essentially irreversible, but takes several thousand seconds. Given this long lifetime, reactions analogous to 4 and 5 can be proposed, which equally well explain the autocatalytic decays reported by Weeks and Rabani:

$$\cdot CO_3^- + HCO_4^- \rightarrow HCO_3^- + \cdot CO_4^- \qquad (22)$$

$$\cdot CO_3^- + CO_4^{2-} \rightarrow CO_3^{2-} + \cdot CO_4^- \qquad (23)$$

As for the case of the superoxide radical product proposed above, a fast radical termination reaction of $\cdot CO_3^-$ with $\cdot CO_4^-$ can be anticipated to double the effect of reactions 22 and 23:

$$\cdot CO_3^- + \cdot CO_4^- \rightarrow C_2O_7^{2-} \qquad (24)$$
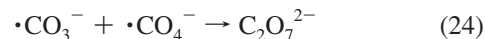
A summary of the proposed mechanism for carbonate growth and decay can be found in Table 2.

To check the behavior of the second-order radical decay in the incomplete $\cdot OH$ scavenging regime, we recorded room temperature (ca. 20 °C) kinetics on a time scale from roughly 1 × 10^{-4} s following nanosecond radiolysis pulses, out to baseline at 0.4 s. Carbonate solutions of 0.005, 0.002, and 0.001 M, and bicarbonate solutions of 0.1, 0.04, and 0.02 M were examined using a range of dose from 4 to 40 Gy.

In Figure 5 we illustrate 600 nm transient absorption data collected to track the decay of $\cdot CO_3^-$ in radiolysis of 0.0025 M carbonate solution. Traces from four consecutive single electron pulses are shown. Similar data are shown in Figure 6 for five consecutive pulses applied to 0.10 M bicarbonate solution. Clearly a product of the radiolysis is formed that accelerates the decay of each subsequent pulse. With enough pulses a steady-state is approached. At lower dose per pulse,
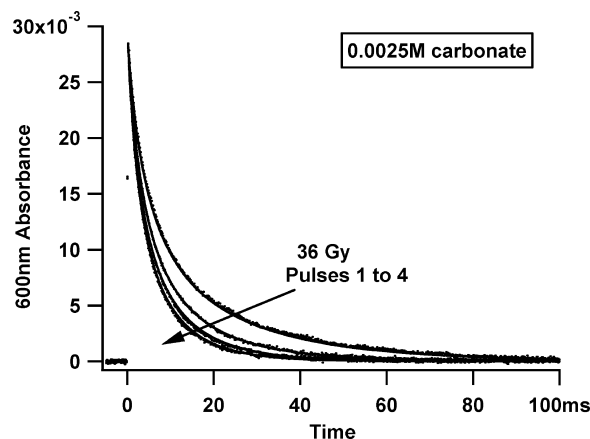
Figure 5. Decay of 600 nm $\cdot CO_3^-$ absorbance in room temperature 0.0025 M carbonate solution, following four consecutive 36 Gy radiolysis pulses. The effect of product buildup with each pulse is easily seen.
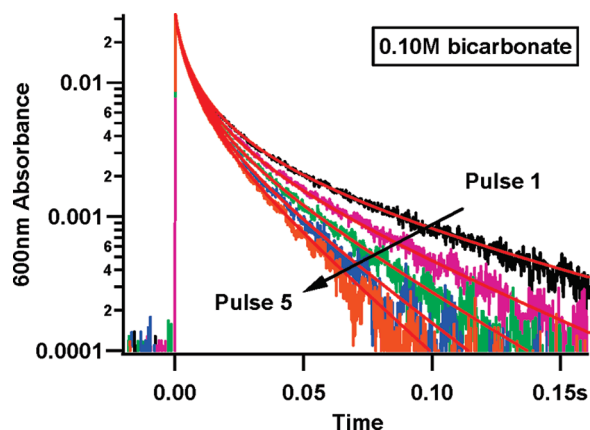

Figure 6. Decay of 600 nm $\cdot CO_3^-$ absorbance in room temperature 0.10 M bicarbonate solution, following five consecutive 35 Gy radiolysis pulses. The effect of product buildup with each pulse is easily seen using the logarithmic amplitude scale.

the effect is diminished proportionally. The additional decay can be qualitatively explained by the total yield of hydrogen peroxide and peroxymonocarbonate product expected via reactions 3a, 16, and 17, which builds up with each pulse. Hydrogen peroxide product alone cannot account for the magnitude of the effect. Given the long lifetime reported for peroxymonocarbonate at room temperature, reactions 22 and 23 apparently contribute or even dominate. However, in our brief study we were not able to find a set of rate constants for the mechanism outlined above, which quantitatively fit all of the decays out to baseline for all reagent concentrations and applied dose. In these long-time experiments, the rise of the absorption at 600 nm was not resolved, and our fitting relied entirely upon the kinetic model and rate constants derived in the previous section to estimate initial concentrations. The observed decays are critically dependent on these starting concentrations. The best fitting parameters found for the six bicarbonate and carbonate solutions are given in Table 2.

The second-order recombination rate constant k_3 was found to change as the carbonate or bicarbonate concentration was changed. We note that reactions 3, 5, 20, and 23 all occur between anions, and therefore are subject to an effect of ionic strength.[36] The relation[36,37]

$$\log(k) = \log(k_0) + 1.02\sqrt{I}/(1 + \sqrt{I})$$

where I is ionic strength and $k_0 = 4.25 \times 10^6$ M^{-1} s^{-1}, was found to apply to reaction 3 and was used as a constraint to guide the global fitting. (We also made one set of measurements in O$_2$-saturated carbonate solution where reaction 20 dominates the decay, and using excess sodium perchlorate salt, confirmed that the equation above applies, with $k_0 = 2.0 \times 10^8$ M^{-1} s^{-1}.) Weeks and Rabani[1] originally reported an effect of ionic strength on reaction 3, but subsequent workers[9,15] reported that there was no obvious ionic strength effect. On the basis of our data and fitting as illustrated in Figures 5 and 6, any given transient decay of $\cdot CO_3^-$ may be a strong mixture of reaction 3, reaction 20, and reactions 4, 5, 22, and 23. It is not surprising that a simple fit of the second-order half-life shows no clear trend versus ionic strength, especially if multiple shots were averaged for a measurement, and if the carbonate/bicarbonate itself is used to adjust ionic strength.

Reaction of $\cdot CO_3^-$ with hydrogen peroxide and/or peroxymonocarbonate appears to be faster in the carbonate solutions than in the bicarbonate solutions (c.f., Table 2). The natural pH of the carbonate solutions is 10.5−11.0, so that a fraction of the hydrogen peroxide exists as the anion HOO$^-$, and a fraction of peroxymonocarbonate as CO$_4^{2-}$. As already noted, reaction 5 is much faster than reaction 4, and from these decays we can infer a similar difference in reactions 22 and 23. The effective combined rate constants k_4 and k_5 recorded in Table 2 are consistent with the pH-dependent measurements of Behar, et al.[2]

Wu et al.[15] reported a significantly shorter apparent second order decay in bicarbonate solutions of 0.001−0.002 m concentration, where less than 15% of the initial $\cdot$OH radicals are scavenged to produce $\cdot CO_3^-$. Similar behavior was reported in carbonate solutions of 0.001−0.002 m at temperatures above 100 °C, where the fraction of scavenged $\cdot$OH is similarly small. We did record decay kinetics in 0.001 m and 0.002 m bicarbonate solutions in our brief kinetics study, but results could not be fit well using parameters identical to those reported for the higher concentration solutions. This is not too surprising given the crude sample-handling arrangements of our experiment. Oxygen was not rigorously excluded. In many samples the effect of adventitious impurities on the decay were clearly apparent. For apparently "good" samples, with very long-lived absorbance out to 0.3 s (for low dose) we noted the same qualitative trend as the Tokyo group, with initial decays significantly shorter than expected from the second-order rate constant k_3.

Simulation of the kinetics in these low-concentration solutions shows that the decay is dominated not by the second-order recombination 3, but by reactions 20, 4, and 5, especially after a first pulse has generated hydrogen peroxide, peroxymonocarbonate, and oxygen. In the presence of a small amount of oxygen (either impurity or generated via reaction 20), hydrogen atoms which constitute some 10% of the initial yield may be converted to superoxide radical and then provide the dominant initial decay channel of $\cdot CO_3^-$ via reaction 20. The simulation in this low-concentration regime is very sensitive to parameters of the scavenging model (i.e., rates for reactions 1, 2, and 16−19) which certainly all have errors in the tens of percent range. A quantitative evaluation of these "incomplete scavenging" systems will require better sample handling and simultaneous recording of both the growth and decay kinetics on the same samples. Nevertheless, we feel confident in ascribing the anomalous second order rate constant results of the Tokyo group to the effect of impurities or multiple pulsing of the samples.

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IV. Conclusion

We have successfully re-evaluated concentration-dependent and temperature-dependent scavenging yield data from Wu et al.[15] to refute the claim that carbonate radical exists as a dimer with its parent carbonate or bicarbonate anion. In so doing, we have estimated the reaction rate for recombination of $\cdot$OH and $\cdot CO_3^-$, which is found to approach a limiting value above 250 °C. We postulate that this results from an "entropic barrier" or steric effect in the energetically downhill recombination reaction.

The complete mechanism of second-order self-recombination of $\cdot CO_3^-$ radicals has heretofore not been conclusively demonstrated. A simple optical measurement of the second-order half-life does not properly describe the chemistry involved. A pre-equilibrium between $\cdot CO_3^-$ and a short-lived dimer $C_2O_6^{2-}$ is strongly indicated based on the slightly negative activation energy for the overall recombination found[16,12,15] below 300 °C. Existing conductivity data[4] is only consistent with production of CO_2 and CO_4^{2-} from this dimer. The present work demonstrates the decay is autocatalytic thanks to reaction of $\cdot CO_3^-$ with the peroxymonocarbonate HCO_4^-/CO_4^{2-} product. In any pulse radiolysis experiment, particularly if $\cdot$OH radicals are incompletely scavenged, reaction of $\cdot CO_3^-$ with hydrogen peroxide also contributes to the decay. Finally, the radicals $\cdot O_2^-$ and $\cdot CO_4^-$ formed respectively from the hydrogen peroxide and peroxymonocarbonate reactions, recombine with $\cdot CO_3^-$.

Supporting Information Available: A PDF is provided containing the following: (A) Algebraic derivation of concentration of all ionic species in "natural-pH" carbonate and bicarbonate solutions up to 250 °C. (B) Ab initio calculations for reaction 3 in gas phase and in polarized continuum. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Weeks, J. L.; Rabani, J. *J. Phys. Chem.* **1966**, *70*, 2100.

(2) Behar, D.; Czapski, G.; Duchovny, I. *J. Phys. Chem.* **1970**, *74*, 2206.

(3) Chen, S.; Cope, V. W.; Hoffman, M. Z. *J. Phys. Chem.* **1973**, *77*, 1111.

(4) Lilie, J.; Hanrahan, R. J.; Henglein, A. *Radiat. Phys. Chem.* **1978**, *11*, 225.

(5) Eriksen, T. E.; Lind, J.; Merenyi, G. *J. Chem. Soc., Faraday Trans. I* **1983**, *79*, 1493.

(6) Lind, J.; Merenyi, G.; Eriksen, T. E. *J. Am. Chem. Soc.* **1983**, *105*, 7655.

(7) Buxton, G. V.; Wood, N. D.; Dyster, S. *J. Chem. Soc., Faraday Trans. I* **1988**, *84*, 1113.

(8) Stanbury, D. M. *Adv. Inorg. Chem.* **1989**, *33*, 69.

(9) Huie, R. E.; Clifton, C. L. *J. Phys. Chem.* **1990**, *94*, 8561.

(10) Bisby, R. H.; Johnson, S. A.; Parker, A. W.; Tavender, S. M. *J. Chem. Soc., Faraday Trans.* **1998**, *94*, 2069.

(11) Czapski, G.; Lymar, S. V.; Schwarz, H. A. *J. Phys. Chem. A* **1999**, *103*, 3447.

(12) Ferry, J. L.; Fox, M. A. *J. Phys. Chem. A* **1999**, *103*, 3438.

(13) Zuo, Z. H.; Cai, Z. L.; Katsumura, Y.; Chitose, N.; Muroya, Y. *Radiat. Phys. Chem.* **1999**, *55*, 15.

(14) Lymar, S. V.; Schwarz, H. A.; Czapski, G. *Radiat. Phys. Chem.* **2000**, *59*, 387.

(15) Wu, G. Z.; Katsumura, Y.; Muroya, Y.; Lin, M.; Morioka, T. *J. Phys. Chem. A* **2002**, *106*, 2430.

(16) Eriksen, T. E.; Lind, J.; Merenyi, G. *Radiat. Phys. Chem.* **1985**, *26*, 197.

(17) Marin, T. W.; Bartels, D. M.; Jonah, C. D.

(18) Takahashi, K.; Cline, J. A.; Bartels, D. M.; Jonah, C. D. *Rev. Sci. Instrum.* **2000**, *71*, 3345.

(19) Cline, J.; Takahashi, K.; Marin, T. W.; Jonah, C. D.; Bartels, D. M. *J. Phys. Chem. A* **2002**, *106*, 12260.

(20) Cline, J. A.; Jonah, C. D.; Bartels, D. M. *Rev. Sci. Instrum.* **2002**, *73*, 3908.

(21) Marin, T. W.; Cline, J. A.; Takahashi, K.; Bartels, D. M.; Jonah, C. D. *J. Phys. Chem. A* **2002**, *106*, 12270.

(22) Bartels, D. M.; Takahashi, K.; Cline, J. A.; Marin, T. W.; Jonah, C. D. *J. Phys. Chem. A* **2005**, *109*, 1299.

(23) Janik, I.; Marin, T.; Jonah, C. D.; Bartels, D. M. *J. Phys. Chem. A* **2007**, *111*, 79.

(24) Marin, T. W.; Takahashi, K.; Jonah, C. D.; Chemerisov, S. D.; Bartels, D. M. *J. Phys. Chem. A* **2007**, *111*, 11540.

(25) Katsumura, Y.; Wu, G. Z.; Lin, M. Z.; Muroya, Y.; Morioka, T.; Terada, Y.; Li, X. F. *Res. Chem. Intermed.* **2001**, *27*, 755.

(26) Elliot, A. J. Rate Constants and G-Values for the Simulation of the Radiolysis of Light Water over the Range 0–300°C; Report AECL-11073, 1994.

(27) Marin, T. W.; Jonah, C. D.; Bartels, D. M. *J. Phys. Chem. A* **2005**, *109*, 1843.

(28) Han, P.; Bartels, D. M. *J. Phys. Chem.* **1990**, *94*, 7294.

(29) Janik, I.; Bartels, D. M.; Jonah, C. D. *J. Phys. Chem. A* **2007**, *111*, 1835.

(30) Frisch, M. J. T., G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, Jr., J. A.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian 03, Revision C.5;02*; Gaussian, Inc.: Wallingford, CT, 2004.

(31) Tomasi, J.; Persico, M. *Chem. Rev.* **1994**, *94*, 2027.

(32) Richardson, D. E.; Regino, C. A. S.; Yao, H. R.; Johnson, J. V. *Free Radical Biol. Med.* **2003**, *35*, 1538.

(33) Regino, C. A. S.; Richardson, D. E. *Inorg. Chim. Acta* **2007**, *360*, 3971.

(34) Bennett, D. A.; Yao, H.; Richardson, D. E. *Inorg. Chem.* **2001**, *40*, 2996.

(35) Richardson, D. E.; Yao, H. R.; Frank, K. M.; Bennett, D. A. *J. Am. Chem. Soc.* **2000**, *122*, 1729.

(36) Weston, R. E.; Schwarz, H. A. *Chemical Kinetics*; Prentice-Hall, Inc.: Englewood Cliffs, NJ, 1972.

(37) Pilling, M. J.; Seakins, P. W. *Reaction Kinetics*; Oxford University Press: Oxford, 1995.

(38) Buxton, G. V.; Greenstock, C. L.; Helman, W. P.; Ross, A. B. *J. Phys. Chem. Ref. Data* **1988**, *17*, 513.