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Acidity of the Carbonate Radical

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A pulse radiolysis study which uses a flow system to irradiate mixtures of H_2CO_3 and HCO_3^- within 50 ms of their formation has demonstrated that the carbonate radical is a strong acid, $pK_a < 0$, contrary to published reports of high pK_as. The rate constant for reaction of the hydroxyl radical with H_2CO_3 is 7×10^4 M^{-1} s^{-1} at about 5 °C.

Introduction

The carbonate radical ion, $CO_3^{\bullet-}$, can be prepared by the reaction of carbonate or bicarbonate ions with the hydroxyl radical:

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

$$OH^{\bullet} + HCO_3^- \rightarrow H_2O + CO_3^{\bullet-} \qquad (2)$$

The rate constant[1] k_1 is 3.0×10^8 M^{-1} s^{-1} but k_2 is only 8.5×10^6, about 40 times smaller. $CO_3^{\bullet-}$ has an absorption spectrum[2,3] with a peak at 600 nm and an extinction coefficient of 1900 M^{-1} cm^{-1}. Chen et al.[4] reported a pK_a for the radical of 9.6, based on a 50% increase in rate constant with pH for reaction of $CO_3^{\bullet-}$ with indole-3-propionate at 0.1 M ionic strength, though no effect was observed at 0 ionic strength. Eriksen et al.[3] reported a range of 7.0 to 8.2 for the pK_a based on an observed increase in absorbance due to the radical with pH at 600 nm. More recently Bisby et al.[5] have used time-resolved resonance Raman spectroscopy to demonstrate that the radical is unprotonated at pH 7.5.

It is well-known that the pK_as of inorganic acids of the type $XO_n(OH)_m$ depend mainly on n, the number of O ligands.[6,7] The reason for this is that the negative charge on the conjugate base can resonate among $n + 1$ presumably equivalent oxygen sites. All acids that have n equal to or greater than 2 are strong acids. Thus, $HCO_3^{\bullet}$ should be as strong an acid as HNO_3 or H_2SO_4, which have pK_as below −1.

The main obstacle to determining the pK_a of $HCO_3^{\bullet}$ is that the HCO_3^-/CO_2 pK_a is 6.37, and so production of CO_2 prevents the use of bicarbonate solutions below about pH 7. However, the first product formed upon reaction of bicarbonate with acid is H_2CO_3. The pK_a of H_2CO_3 is 3.5 and its half-life for dissociation to CO_2 is 50 ms at 25 °C and 380 ms at 0 °C below pH 1.[8] The lifetime is longer at higher pH. Thus, large concentrations of HCO_3^- and H_2CO_3 can be transiently produced in the acid range for a pulse radiolysis study by rapidly mixing solutions of bicarbonate and buffers or acid and flowing the mixture through the pulse radiolysis cell. With this technique, the $CO_3^{\bullet-}$ absorption was observed and studied down to nearly pH 0.

Experimental Section

The flow system has been described earlier.[9] Briefly, a pair of 2.5 cm^3 syringes were emptied by a pneumatic drive, the contents flowing into a mixer and then through a 3 mm i.d. cell with a 2 cm light path length. The cell was irradiated with 2 MeV electrons while the solution was still flowing. The apparatus was used without a stop syringe, as the time required for the experiment (a maximum of 300 μs) was much shorter than the flow time through the cell. The flow rate from the syringes was determined to be 6.3 cm^3/s each, with the solutions at either room temperature or 5 °C, by measurement of a video recording with 100:1 time expansion. The subsequent “dead” volume, including mixer, tubing, and half the cell volume, was 0.47 cm^3 which, with the flow rates, leads to a dead-time estimate of 37 ms. A separate estimate, in which ferric ion and thiocyanate were mixed,[10] gave an estimated dead time of 51 ms from the rate constant for $FeSCN^{2+}$ formation and the ratio of absorbance during flow to absorbance of a fully equilibrated solution. Since these times are comparable to the H_2CO_3 lifetime at room temperature, both the bicarbonate and the acid solutions were equilibrated with ice baths before the syringes were filled and pulsed. A nominal temperature of 5 °C was assigned to the solutions to allow for warming during the filling, mixing, and flowing. The apparatus was conditioned by multiple fillings at 6 s per filling before data were collected. The apparatus dead time and the half-life at 5 °C (250 ms) would indicate that about 10% to 15% of the total carbonate may have decomposed in solutions below pH 1. Only the rate constant measured in this range would be affected and no correction has been made. The H_2CO_3 half-lives at higher pH values are longer and the effect would be smaller (possibly 5% at pH 3.4).

The pulse radiolysis was performed with 2 MeV electrons from a Van de Graaff accelerator using optical detection. A xenon arc light source was used, with and without pulsing. Most of the work involved rather small absorption signals (absorbance < 0.02) and so signals were averaged over 3−15 pulses to increase accuracy (one pulse per sample). Dosimetry was

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performed with N_2O-saturated 0.01 M KSCN solution using $G\epsilon = 4.84 \times 10^4$ ions $(100\ \mathrm{eV})^{-1}\ \mathrm{M}^{-1}\ \mathrm{cm}^{-1}$ at 472 nm.

The $HClO_4$ was GFS "double distilled from Vycor" grade. All other reagents were analytical grade, except for some of the sodium bicarbonate, which was purified by fractional recrystallization when used for experiments at pH below 1. Several methods were used to maintain pH. A 1:1 mixture of carbonate to bicarbonate was used at pH 10. 0.01 M phosphate buffers in one syringe were mixed with bicarbonate in the other at pH 6 to pH 8. Sulfuric acid solution was mixed with bicarbonate to obtain pH 3.4 to pH 5, and perchloric acid solutions were mixed with bicarbonate to produce the lower pHs. The pH values from 2.7 to 5 were calculated from solution composition and the pK of H_2CO_3 (3.5).

Results

The usual method of studying hydroxyl radical reactions is to saturate the solution with N_2O, which produces $OH^\bullet$ by reaction with solvated electrons. With the $OH^\bullet$ produced directly from the water, the $OH^\bullet$ yield is 90% of all radicals (the remaining 10% is $H^\bullet$). This method would not work here as most of the solutions have very high acid concentrations, and e_{aq}^- would react with H^+ to produce $H^\bullet$ which is relatively inert to N_2O. Instead, air-saturated solutions were used, in which case both e_{aq}^- and $H^\bullet$ react to form $HO_2^\bullet$, which is inert to carbonate. The yield of $OH^\bullet$ available to react with carbonate in a 0.01 M solution saturated with air is expected to be about 2.9 radicals per 100 eV absorbed.[11] The actual yield was measured by a direct comparison between N_2O-saturated and air-saturated solutions. The yield of $CO_3^{\bullet-}$ in N_2O-saturated solution containing 0.01 M Na_2CO_3 at pH 10 should be the same as the $(SCN)_2^{\bullet-}$ yield in the standard N_2O-saturated 0.01 M KSCN dosimeter solution, 6.13 radicals per 100 eV.[12] Direct comparison with the dosimeter gave the extinction coefficient of $CO_3^{\bullet-}$ as 1925 $\mathrm{M}^{-1}\ \mathrm{cm}^{-1}$ at 600 nm, which is in good agreement with the published values.[2,3] The ratio of the absorbance obtained when the same solution was irradiated air-saturated to that obtained after N_2O saturation was 0.486, which corresponds to a yield of 2.98 ions per 100 eV for $CO_3^{\bullet-}$ in air-saturated solution.

The pK_a of HCO_3^- is 10 at 0.1 M ionic strength; therefore, over the pH range from 8 down to at least 2 the principal species reacting with $OH^\bullet$ is HCO_3^-, reaction 2. This reaction is so slow that radical−radical reactions can compete even in 0.2 M HCO_3^-. Most of the radical−radical reactions are known and measured rate constants exist. It is unnecessary, however, to rely on numerical integration of the rate equations describing the complete mechanism in order to extract the $CO_3^{\bullet-}$ extinction coefficients. Instead, the radical−radical reactions will be represented by the simplified scheme

$$OH^\bullet + R \rightarrow \text{products} \tag{3}$$

$$CO_3^{\bullet-} + R \rightarrow \text{products} \tag{4}$$

The generalized radical R should properly be considered a weighted sum of $HO_2^\bullet$ (or $O_2^{\bullet-}$ above pH 5), $H^\bullet$, e_{aq}^-, $OH^\bullet$, and $CO_3^{\bullet-}$, but in order to obtain an approximate analytical solution of the $CO_3^{\bullet-}$ rate equation, the concentration of R will be assumed constant. This solution should become accurate as [R] approaches zero, and the form of the equation suggests the proper method to extrapolate the results to zero [R]. Actually, R is primarily the $HO_2^\bullet$ radical. The formation of $HO_2^\bullet$ from reaction of oxygen with $H^\bullet$ and e_{aq}^- (yields of 0.6 and 2.8 radicals per 100 eV) is at least 5 times as rapid as reaction 2 in all cases, and so $HO_2^\bullet$ can be treated as if it were a primary product with a yield of 3.4. Furthermore, since $HO_2^\bullet$ is in excess of $OH^\bullet$ and $CO_3^{\bullet-}$, and reactions 3 and 4 are minor processes, the approximation that R is constant during $CO_3^{\bullet-}$ formation is reasonable. With this approximation, and with the fact that $CO_3^{\bullet-}$ is the only species present which absorbs light at 600 nm, the integration of the rate equations derived from reactions 2−4 gives

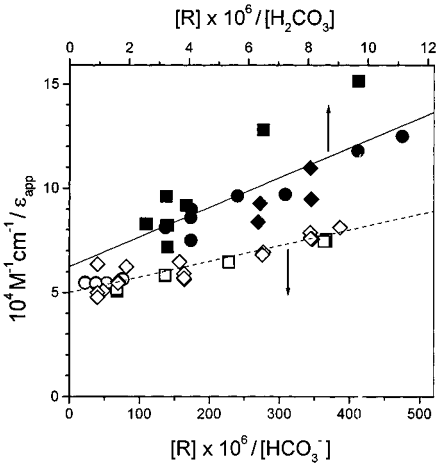

Figure 1. Variation of reciprocal apparent extinction coefficient at 600 nm with the ratio of the initial radical concentration to the dominant form of carbonate. Lower curve (open symbols) is for the pH region in which reaction 2 dominates (see eq 6): squares, 0.1 M total carbonate, pH 3.9; circles, 0.25 M total carbonate, pH 3.5; diamonds, 0.25 M total carbonate, pH 2.7. Upper curve (closed symbols) is the pH region in which reaction 8 dominates (see eq 9): squares, 0.45 M total carbonate, pH 0.8; circles, 0.45 M total carbonate, pH 0.26; diamonds, 0.22 M total carbonate, pH 0.11.

$$A = l\epsilon_{\mathrm{app}}[OH^\bullet][\exp(-k_4[R]t) - \exp(-k_{\mathrm{obsd}}t)] \tag{5}$$

in which A is the absorbance, $l\epsilon[CO_3^{\bullet-}]$, l is the optical path length, ϵ is the average extinction coefficient for the mixture of $CO_3^{\bullet-}$ and $HCO_3^\bullet$ present at any pH, ϵ_{app} is defined as

$$\epsilon_{\mathrm{app}} = \frac{\epsilon}{1 + \dfrac{k_3 - k_4}{k_2[HCO_3^-]}[R]} \tag{6}$$

and k_{obsd} is defined as

$$k_{\mathrm{obsd}} = k_2[HCO_3^-] + k_3[R] \tag{7}$$

The kinetic data were all fit to eq 5, from which the three parameters k_4[R], k_{obsd}, and ϵ_{app} were derived. The disappearance of $CO_3^{\bullet-}$ $(-k_4[R]t)$ was followed for about 5% to 20% of the decay.

According to eq 6, $1/\epsilon_{\mathrm{app}}$ should increase linearly with $[R]/[HCO_3^-]$, and this effect is shown for data from solutions between pH 2.7 and pH 3.9 as the lower curve in Figure 1. The HCO_3^- concentrations covered the range of 0.034−0.25 M. From the intercept, the average ϵ in this pH region is 2000 M^{-1} cm^{-1}. Data at higher pHs, from 5 through 8, were analyzed separately, as the $O_2^{\bullet-}$ radical, with a pK_a of 4.8,[13] is dominant in this region. A similar straight line was found but with a slope that was 19% smaller than that at pH 2.7 through 3.9 (data not shown). The ϵ in the higher pH region was 1955 $\mathrm{M}^{-1}\ \mathrm{cm}^{-1}$.

These extinction coefficients are averages for each pH region. Extinction coefficients at each pH were obtained from similar plots to Figure 1 with just the data at that pH, but using the commonly obtained slope to extrapolate to the intercept. The resulting data are shown in Figure 2 as the ratio of ϵ at each pH to $\epsilon(CO_3^{\bullet-})$. If it were assumed that only the basic form of the radical, $CO_3^{\bullet-}$, absorbs at 600 nm, then this ratio would be the fraction of the radical present as $CO_3^{\bullet-}$. The inset in Figure 2 is the spectrum observed at several acidities. There is no change in spectral shape or position between pH 10 and 2.7.

$k_{obsd}/[HCO_3^-]$ was found to increase linearly with $[R]/[HCO_3^-]$ as predicted by eq 7 (data not shown). The intercept, k_2, was 5.0×10^6 M^{-1} s^{-1} at pH 2.7−3.9 and 5.2×10^6 M^{-1} s^{-1} at the higher pHs. The "recommended" value is 8.5×10^6 at 25 °C, and the activation energy has been measured to be 5.1 kcal/mol, so the predicted k_2 is 4.6×10^6 at 5 °C, within 10% of our value.

When a much more acidic solution, one containing 0.6 M $HClO_4$ after mixing, was pulse-irradiated, a small growth and decay of absorption was seen. This solution contained 0.45 M H_2CO_3, and since the pK_a of H_2CO_3 is 3.5, the residual amount of HCO_3^- (2×10^{-4} M) could account for less than 10% of the reaction seen. Most of the $CO_3^{\bullet-}$ must be produced in the reaction

$$OH^{\bullet} + H_2CO_3 \rightarrow H_2O + H^+ + CO_3^{\bullet-} \qquad (8)$$

This reaction is much slower than reaction 2, and so radical−radical reactions are very important and only small absorbances can be obtained. In fact, in all solutions studied here below pH 1, the largest absorbance observed was 0.004 and the average absorbance was 0.002. The noise levels were quite high but substantial results could be obtained. The reaction rates were small enough that the presence of a trace impurity, at 10 ppm, say, in the bicarbonate, could influence the results. The bicarbonate was recrystallized once, as described in the Experimental Section, and a 15% increase in absorbance over a similar solution prepared from unpurified bicarbonate was observed. All work reported here was done with the purified material.

The data obtained below pH 1 were fit to eq 5, but with ϵ_{app} and k_{obsd} now defined as

$$\epsilon_{app} = \frac{\epsilon}{1 + \dfrac{k_3 - k_4}{k_8[H_2CO_3]}[R]} \qquad (9)$$

$$k_{obsd} = k_8[H_2CO_3] + k_3[R] \qquad (10)$$

A plot of $1/\epsilon_{app}$ vs $[R]/[H_2CO_3]$, as suggested by eq 9, is shown as the upper curve in Figure 1. The intercept is larger than at the higher pH, possibly indicating a reduced ϵ, but it is obvious that the experimental error is large enough to encompass the same intercept at pHs below 1 as was observed at pHs above 2.5. Note that whereas the extrapolations to 0 dose were only over the last 5% at pHs above 2.5, they were over 40% at pHs below 1. As was done in the other pH regions, separate values of the extinction coefficients at the three acidities below pH 1 were obtained by applying the slope from the upper curve of Figure 1 to each acidity separately. These values are shown in Figure 2 (the data below pH 1). There may be a small falloff in apparent extinction coefficient in this region (15 to 20%) but the spectrum, shown in the inset to Figure 2, has the same shape as that of the $CO_3^{\bullet-}$ radical. The possible falloff could be due to (a) extrapolation error, (b) residual impurity effect, or (c) a real effect demonstrating the onset of a pK_a "titration" curve. Even if (c) is correct, and only $CO_3^{\bullet-}$ is assumed to absorb at 600 nm, it can be concluded from the data in Figure 2 that the pK_a of $HCO_3^{\bullet}$ is <0.

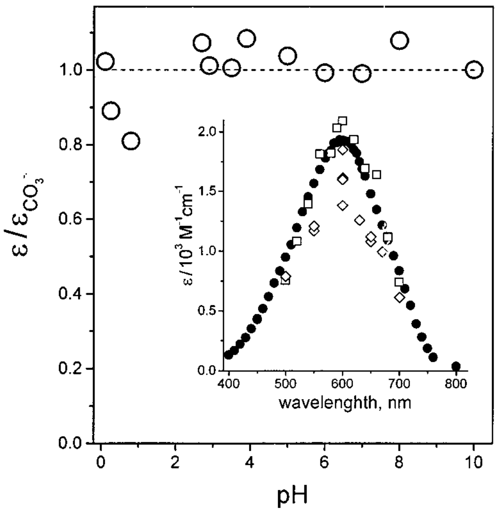

Figure 2. Fraction of total carbonate radical which is present as the basic form, $CO_3^{\bullet-}$, as a function of the pH. Inset: The spectrum observed at pH 10 (filled circles), at pH 2.7 (open squares), and pH 0.8 (open diamonds).

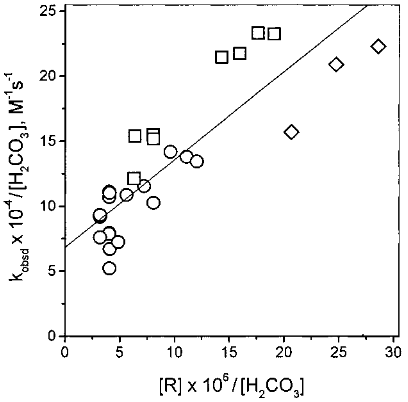

Figure 3. Determination of the rate constant for reaction 8. Values of k_{obsd} are plotted vs initial radical concentration in manner suggested by eq 10: circles, 0.45 M H_2CO_3 at pH 0.8 and 0.26; squares, 0.23 M H_2CO_3 at pH 0.11; diamonds, 0.1 M H_2CO_3 at pH 0.1. The slope shown was obtained from similar data at higher pH (2.7 to 3.9), from which k_2 was determined.

The rate constant for reaction 8 can be found by plotting $k_{obsd}/[H_2CO_3]$ vs $[R]/[H_2CO_3]$ as suggested by eq 10. If eq 10 is compared to eq 7, it is clear that the slope of the plot should be the same at all pH values below the pK_a of $HO_2^{\bullet}$ (4.8).[13] The data are shown in Figure 3 where the slope drawn is that obtained from the results at pH 2.7−3.9. It is found that k_8 is 7×10^4 M^{-1} s^{-1}, which is 75 times smaller than k_2. This is in satisfactory agreement with the ratio of slopes (85) from the two lines in Figure 1.

Meaningful $CO_3^{\bullet-}$ decay data could be obtained in the low pH region, due to use of a longer time scale and the fact that the Xe lamp was not pulsed for these studies. The value of k_4 obtained from the $-k_4[R]t$ term of eq 5 was 1.1×10^9 M^{-1} s^{-1}. Because of the fact that $CO_3^{\bullet-}$ and $HO_2^{\bullet}$ are the only significant radicals left at this time, and that the reactions of $2CO_3^{\bullet-}$ and $2HO_2^{\bullet}$ are slow enough to be ignored, this rate constant should be a good estimate for k_{11} at 5 °C.

$$CO_3^{\bullet-} + HO_2^{\bullet} \rightarrow \text{products} \qquad (11)$$

Estimates of k_3 may be obtained from the slope-to-intercept ratios of Figure 1 using the values of k_2, k_4, and k_8 obtained above (eqs 6 and 9). The upper curve yields 6.8×10^9 M^{-1} s^{-1} and the lower curve gives 7.2×10^9 M^{-1} s^{-1}. k_3 may also be obtained from the slope of the rate constant curve in Figure 3 (eq 7 or 10), which yields 6.7×10^9 M^{-1} s^{-1}. The assumptions made in the derivation of eq 5 lead to the expectation that k_3 should be largely determined by the rate constant for $OH^\bullet + HO_2^\bullet \rightarrow$ product, which has been reported to be 1×10^{10} M^{-1} s^{-1}at room temperature.[15] These values of k_3 should not be taken as measurements of the $HO_2^\bullet$ rate constant, because the treatment is only approximate; however, the agreement adds confidence to the use of the approximation.

Discussion

It is clear from the results presented here that $HCO_3^\bullet$ is a strong acid. An explanation for the earlier high pK_a values is not so clear. Eriksen et al.[3] pulse-irradiated air-saturated solutions at constant ionic strength of 0.1 M, that is, $[HCO_3^-] + 3[CO_3^{2-}] = 0.1$ M, and doses of 35 Gy (i.e., the initial $[OH^\bullet]$ was 10.5 μM, and $[O_2^{\bullet -}]$ from $H^\bullet$ and e_{aq}^- was 12.3 μM). They found that the ratios of the apparent extinction coefficients at various pHs to that of $CO_3^{\bullet -}$ decreased with decreasing pH. For instance, it was 0.72 at pH 8 and 0.56 at pH 7. They interpreted this decrease as the onset to the pK_a. An alternate explanation might be that since reaction 1 is 40 times faster than reaction 2, the rate of formation of $CO_3^{\bullet -}$ decreases strongly with decreasing pH while the radical−radical reaction rates do not change much. It is thus expected that the yield of $CO_3^{\bullet -}$ will decrease with decreasing pH and it is tempting to conclude that this explains their results. However, Holcman et al.[14] have performed a numerical integration of the rate equations which describe this system and find the calculated decrease of apparent extinction coefficient to be only about half that observed by Eriksen et al. They calculate that the fraction of $OH^\bullet$ which reacts to form $CO_3^{\bullet -}$ should be 0.83 and 0.76 at pH 8 and pH 7. We have repeated the calculations with slightly different rate constants from different sources and obtained essentially the same results, namely 0.85 and 0.79 at pH 8 and pH 7. It would require factor of 2 increases in each radical−radical rate constants to account for the results of Eriksen et al., which is not reasonable.

Some of our data reported in Figure 1 were obtained in the same pH, concentration, and dose ranges that were used by Eriksen et al., that is 0.1 M HCO_3^- and 35 Gy. A comparison of the maximum absorbance obtained in our absorbance−time curves with that expected for pure $CO_3^{\bullet -}$ gave ratios of 0.86 at pH 8 and 0.77 at 7. This is also about half the effect observed by Eriksen et al. but agrees well with the expectations from numerical integration. The reason for the discrepancy in results is not clear but must involve the different methods of solution preparation.

Chen et al.[4] found that the effect of ionic strength on certain reactions of $CO_3^{\bullet -}$ with negatively charged ions varies with ionic strength in a fashion which suggested to them that the radical was negatively charged in basic solution but not at pH 7−8. They concluded that the pK_a of $HCO_3^\bullet$ was 9.6 from the variation of the effect with pH. However, the acid and base forms of a species with such a high pK_a should exhibit widely different rate constants for reactions at low ionic strength or with neutral species, and their spectra should exhibit appreciable spectral shifts. They found neither of these effects, and so a low pK_a is in good agreement with most of their results, though it leaves the ionic strength effects to be explained.

The rate constants observed for reactions 2 and 8 by themselves suggest that $HCO_3^\bullet$ is a strong acid. These reactions are likely to be hydrogen abstraction reactions, and the ratio $k_2/k_8 = 80$ suggests that leaving a proton on the product radical is strongly destabilizing compared to the proton on the reactant, which has a pK_a of 3.5.

Conclusions

$HCO_3^\bullet$ is a strong acid (p$K_a < 0$) and can be prepared in acidic solution by reaction of $OH^\bullet$ with H_2CO_3 (though not efficiently). All rate constants, most of which have been determined in basic solution, can be applied throughout the pH range from 0 to 14 without change.

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