The Hidden Equilibrium in Aqueous Sodium Carbonate Solutions − Evidence for the Formation of the Dicarbonate Anion

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Crossover ^{13}C NMR experiments between [^{13}C]carbonate and [^{18}O]carbonate in aqueous solution confirm the combined action of two oxygen-exchange modes. The isotopomeric carbon dioxides formed in the hydrolysis equilibrium of the labeled carbonate anions react with hydroxide with formation of hydrogencarbonate and with isotopomeric carbonate anions yielding the corresponding dicarbonate species, which, in the back reaction, form carbon dioxide and carbonate anions with distributed oxygen.

Introduction

In aqueous solutions of metal carbonates the carbonate ion suffers from partial hydrolysis into hydrogencarbonate, carbonic acid and dissolved carbon dioxide [reactions (1)−(4)]. An impressive number of techniques have been applied to determine the rate and equilibrium constants of the reaction steps involved. Much of this data has been collected.[1] Because of its kinetic instability in the presence of water,[2] the fraction of the solvated carbon dioxide present as carbonic acid is less than 1%.[3] From the first (apparent) and the second dissociation constant of "carbonic acid", and the ion product of water, the dependence of the composition of the $CO_2/HCO_3^-/CO_3^{2-}$ system on the pH value can be calculated. For example, a 0.01 M solution of sodium carbonate exhibits a pH value of 11.16 and the molar fractions of carbonic species are $x_{CO_3^{2-}} = 0.86$, $x_{HCO_3^-} = 0.14$ and $x_{CO_2} = 3 \times 10^{-6}$.

$$(1)\quad CO_3^{2-} + H_2O \rightleftharpoons HCO_3^- + OH^-$$

$$(2)\quad HCO_3^- + H_2O \rightleftharpoons H_2CO_3 + OH^-$$

$$(3)\quad H_2CO_3 \rightleftharpoons CO_2 + H_2O$$

$$(4)\quad HCO_3^- \rightleftharpoons CO_2 + OH^-$$

As shown in the pioneering work of Mills and Urey,[4] carbonate dissolved in ^{18}O-enriched water slowly exchanges its oxygen atoms with the oxygen atoms of the water. The rate of this oxygen exchange is mainly governed by the addition of hydroxide to carbon dioxide.[4,5] Himmelblau and Babb[6] have studied the rate of this reaction step by adding ^{14}C-labeled hydrogencarbonate to unlabeled hydrogencarbonate/CO_2 solutions and observing the appearance of $^{14}CO_2$. The values obtained by this method for the hydroxylation of carbon dioxide are much higher than those found by other techniques. This discrepancy points to a superimposition of an oxygen-exchange process between carbonic species.[7,8] A kind of molecular complex, written as $CO_2{\cdot}OH^-$ and supposed to be distinctly separated from HCO_3^- and $CO_2 + OH^-$, has been suggested for this purpose.[7] It is assumed that this complex is able to transfer OH^- to a second CO_2 molecule. The occurrence of cyclic oligomeric orthocarbonic acid was also proposed to account for the oxygen-transfer process.[8]

Tu and Silverman[9] have studied the kinetics of the oxygen exchange by adding ^{18}O-labeled carbonate to solutions containing ^{13}C-enriched carbonate. The rate of appearance of ^{18}O in the ^{13}C-enriched species was measured by mass spectrometry at pH values ranging from 8 to 10. A kinetic analysis revealed that the oxygen transfer can be described by the overall reaction (5).

$$(5)\quad {}^{13}CO_2 + C^{18}O_3^{2-} \rightleftharpoons {}^{13}CO_2{}^{18}O^{2-} + C^{18}O_2$$

The rate of the second-order reaction (5) was found to be competitive with the rate of the back-reaction (4). Therefore, the carbonate oxygen atoms are simultaneously exchanged between carbonic species [reaction (5)] and with the solvent water [reaction (4)].

In this contribution the parallel occurrence of two oxygen-exchange modes is directly observed by NMR spectroscopy and explained by a competitive addition of hydroxide and carbonate ions to carbon dioxide.

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Results

Sodium [$^{18}O_3$]carbonate was prepared from tetraethyl orthocarbonate by stepwise hydrolysis with [^{18}O]water. The first acid-catalyzed step yields diethyl [carbonyl-^{18}O]carbonate, which was further transformed into sodium [^{18}O]carbonate by saponification. According to ^{13}C NMR measurements the sodium carbonate obtained consists of about 46% [$^{18}O_3$], 41% [$^{18}O_2$], 12% [^{18}O] and 1% unlabeled carbonate. This corresponds to an ^{18}O content in the water of 77%. The isotopic enrichment of the water used for hydrolysis was determined to be 80% ^{18}O. The somewhat lower value in the reaction product results from the presence of traces of [^{16}O]water during the synthetic procedure.

The distribution of the isotopomeric carbonate species could be established by ^{13}C NMR spectroscopy. The ^{18}O isotope bound to C causes a small high-field shift of the ^{13}C resonance frequency relative to the ^{16}O compound.[10] The ^{18}O isotope effect on the ^{13}C chemical shift is additive. Therefore, the four isotopomeric species $C^{18}O_{3-n}O_n^{2-}$ (n = 0, 1, 2, 3) should produce four equidistantly separated signals. The carbonyl-^{13}C resonances in ketones, aldehydes, esters and carboxylic acids are shifted up-field by about 0.05,[10b] 0.04,[10b] 0.04,[10b] and 0.03 ppm,[10b] respectively, when replacing ^{16}O by ^{18}O. Because of the lower double-bond character in the carbonate ion, a value of $\Delta\delta$ = 0.02 ppm per ^{18}O is expected (see Supporting Information for more details).

The ^{13}C NMR spectrum was measured in D_2O containing 1 equiv. of NaOD per ^{18}O-labeled Na_2CO_3. Under these conditions the relative amount of ^{18}O-labeled CO_2, formed according to the hydrolysis equilibrium in reactions (1)−(4), is suppressed by about two orders of magnitude and, thus, the oxygen exchange is slowed down. Indeed, repeated measurements within 12 h produced spectra with four signals separated by 0.016 ppm, with no detectable changes in their relative intensities.

In contrast, the ^{13}C NMR spectra of a 0.44 M solution in pure D_2O measured over several weeks showed an exchange of the oxygen atoms of the carbonate ion with the oxygen atoms of the solvent D_2O. Some selected examples are presented in Figure 1. It becomes evident that the carbonate species, separated by 0.018 ppm according to the number of incorporated ^{18}O atoms, lose the heavier oxygen atoms successively. After standing at 20 °C for 100 d, the carbonate consists of about 92% $C^{16}O_3^{2-}$. This is near the calculated end-point for statistical distribution of oxygen atoms from the labeled carbonate and the solvent D_2O (93.28% $^{16}O_3$, 6.59% $^{16}O_2{}^{18}O$, 0.15% $^{16}O^{18}O_2$, 0.001% $^{18}O_3$).

The intermolecular oxygen transfer between carbonic species was examined by means of a crossover experiment. A solution of 1 mg of sodium [^{13}C]carbonate (99% ^{13}C) and 31 mg of the ^{18}O-labeled sodium carbonate in 600 μL of D_2O was subjected to ^{13}C NMR spectroscopy. At t = 0 this solution is composed of 43.49% $Na_2C^{18}O_3$, 39.46% $Na_2C^{18}O_2{}^{16}O$, 11.75% $Na_2C^{18}O^{16}O_2$, 1.04% $Na_2C^{16}O_3$, 0.48% $Na_2{}^{13}C^{18}O_3$, 0.43% $Na_2{}^{13}C^{18}O_2{}^{16}O$, 0.13% $Na_2{}^{13}C^{18}O^{16}O_2$, and 3.19% $Na_2{}^{13}C^{16}O_3$. The total carbonate concentration is 0.48 M. The ^{13}C,^{18}O-containing species result from the natural ^{13}C content in the ^{18}O-labeled carbonate. The ^{13}C-labeled isotopomers of this mixture amount to 4.23% of total carbonate and contribute to the ^{13}C NMR spectrum. The calculated ratio of the NMR-active isotopomers at t = 0 is: $^{13}C^{16}O_3^{2-}$/$^{13}C^{16}O_2{}^{18}O^{2-}$/$^{13}C^{16}O^{18}O_2^{2-}$/$^{13}C^{18}O_3^{2-}$ = 74.3:3.1:10.6:12.0. After infinite time, the total amount of ^{18}O and ^{16}O incorporated in the solution by the isotopomeric carbonates and D_2O should be statistically distributed. The resulting ratio of $^{13}C^{16}O_3^{2-}$/$^{13}C^{16}O_2{}^{18}O^{2-}$/$^{13}C^{16}O^{18}O_2^{2-}$ was calculated to be 94.1:5.8:0.1.

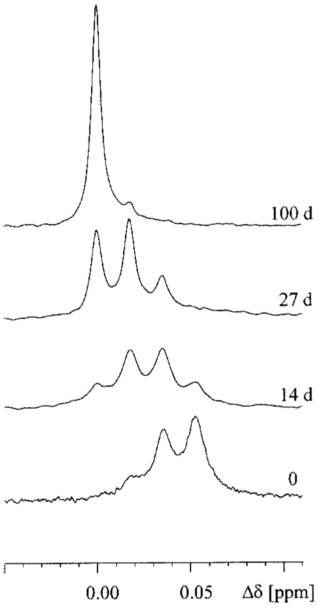


Figure 1. Time-dependent ^{13}C NMR spectra of a 0.44 M solution of $Na_2C^{18}O_{3-n}O_n^{2-}$ in D_2O at 20 °C

Provided that the statistical distribution is caused only by oxygen exchange between carbonic species and D_2O, this end-point should be approached in a monotonic manner. Inspection of the ^{13}C NMR measurements over a period of 154 d obviously reveals that this is not the case. Some representative measurements are given in Figure 2 (the complete set of data in form of schematic diagrams showing the relative amounts of $^{13}C^{16}O_{3-n}{}^{18}O_n^{2-}$ isotopomers as a function of time can be found in the Supporting Information).

The relative amounts of the four isotopomers $^{13}C^{16}O_{3-n}{}^{18}O_n^{2-}$ (n = 0−3) are plotted against time in Figure 3. It can be seen that the relative amount of $^{13}C^{16}O_3^{2-}$ decreases from 74% to a minimum of about 25% within 16 d. It then steadily increases again and slowly approaches the calculated end-point. On the other hand the curve representing $^{13}C^{16}O_2{}^{18}O^{2-}$ increases at the beginning and then reaches a plateau before slowly declining after about 25 d. The relative amount of $^{13}C^{16}O^{18}O_2^{2-}$ also passes through a maximum after about 15 d.

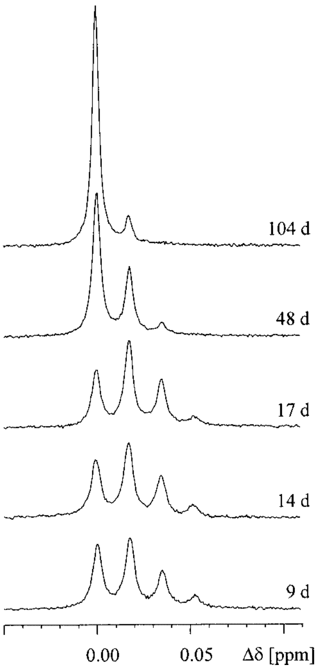


Figure 2. Time-dependent ^{13}C NMR spectra of a 0.48 M solution of a mixture (initial composition see text) of ^{13}C- and ^{18}O-labeled sodium carbonate in D_2O

Discussion

The change of the relative intensities of the $^{13}C^{16}O_{3-n}{}^{18}O_n{}^{2-}$ species present in the carbonate mixture prepared from [^{13}C]- and [^{18}O]-labeled sodium carbonate indicates the parallel operation of two oxygen-exchange modes. At the beginning the vast majority of the carbonate consists of $^{12}C^{18}O_3{}^{2-}$ and $^{12}C^{16}O^{18}O_2{}^{2-}$. At this stage the overall reactions (5) and (5′) contribute mainly to the appearance of the ^{13}C NMR spectra.

$$(1') \quad {}^{13}CO_3{}^{2-} + D_2O \rightleftharpoons D^{13}CO_3{}^{-} + OD^{-}$$

$$(4') \quad D^{13}CO_3{}^{-} \rightleftharpoons {}^{13}CO_2 + OD^{-}$$

$$(5) \quad {}^{13}CO_2 + C^{18}O_3{}^{2-} \rightleftharpoons {}^{13}C^{18}O_2O^{2-} + C^{18}O_2$$

$$(5') \quad {}^{13}CO_2 + CO^{18}O_2{}^{2-} \rightleftharpoons {}^{13}CO_2{}^{18}O^{2-} + CO^{18}O$$

Parallel to these exchange processes the ^{18}O-labeled carbonates, added as $^{12}C^{18}O_{3-n}{}^{16}O_n{}^{2-}$ or formed in the meantime as $^{13}C^{16}O_{3-n}{}^{18}O_n{}^{2-}$, lose ^{18}O as the result of the hydrolysis sequence [reactions (1′′) and (4′′)]. The [^{18}O]hydroxide ions expelled rapidly equilibrate with the large ^{16}O stock of the solvent D_2O [reaction (6)]; thus, in the back-reaction (hydroxylation of isotopomeric carbon dioxides) mainly ^{16}O is introduced. Therefore, the carbonic species are continuously depleted of their ^{18}O labeling. This reduces the amount of $^{12}C^{18}O_{3-n}{}^{16}O_n{}^{2-}$ species capable of transferring ^{18}O to $^{13}CO_2$, and the $^{13}C^{16}O_{3-n}{}^{18}O_n{}^{2-}$ species produced in the meantime will be degraded again. Therefore, as the reaction progresses the intensity of $^{13}C^{16}O_3{}^{2-}$ passes through a minimum before it steadily increases towards the value of about 94% calculated for the statistical distribution.

The direct observation of the oxygen-exchange processes in aqueous carbonate solution by ^{13}C NMR spectroscopy confirm the conclusion of Tu and Silverman.[9] The well-established up-take of oxygen atoms from water has to be combined with a process of transferring oxygen atoms be-

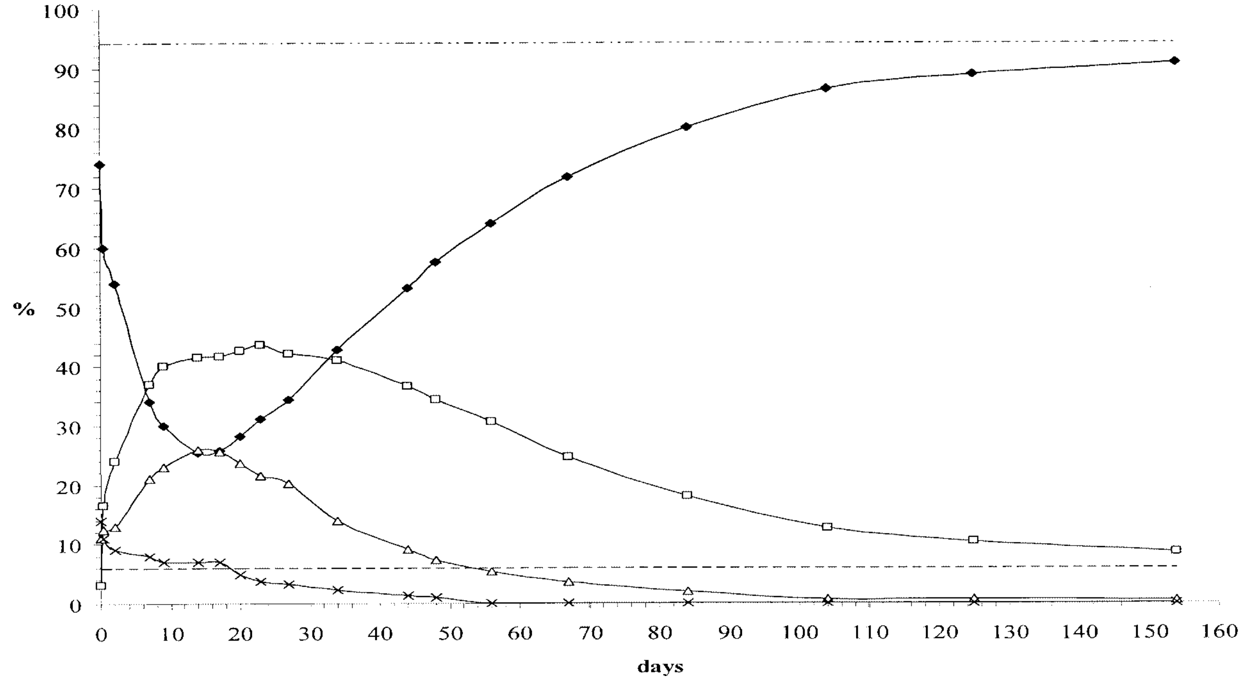


Figure 3. Change of the concentration of [^{13}C]carbonate species as a function of time (black diamonds: $^{13}C^{16}O_3{}^{2-}$; squares: $^{13}C^{16}O_2{}^{18}O^{2-}$; triangles: $^{13}C^{16}O^{18}O_2{}^{2-}$; X: $^{13}C^{18}O_3{}^{2-}$; – - - – : calculated end-point for $^{13}C^{16}O_3{}^{2-}$; – – – : calculated end-point for $^{13}C^{16}O_2{}^{18}O^{2-}$

tween carbonic species. The latter process remains hidden unless crossover experiments between carbon- and oxygen-labeled isotopomers of carbonate are performed.

(1'') ${}^{13}CO_2{}^{18}O^{2-} + D_2O \rightleftharpoons D^{13}CO_2{}^{18}O^- + OD^-$

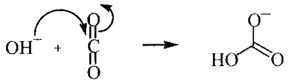
(4'') $D^{13}CO_2{}^{18}O^- \rightleftharpoons {}^{13}CO_2 + {}^{18}OD^-$

(4''') $D^{13}CO_2{}^{18}O^- \rightleftharpoons {}^{13}CO^{18}O + OD^-$

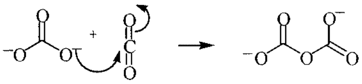
(6) ${}^{18}OD^- + D_2O \rightleftharpoons D_2{}^{18}O + OD^-$

In terms of reaction mechanisms the hydroxylation of carbon dioxide is a nucleophilic addition of hydroxide to a carbonyl group, as shown in reaction (7). For reactions of this type the basicity is a main factor for determining the nucleophilic power of the nucleophiles.[11] From the nucleophiles present in an aqueous carbonate solution the CO_3^{2-} anion (pK_a = 10.33) is nearest to the OH^- ion (pK_a = 15.74) in its basicity. The addition of carbonate to CO_2 would lead to the dicarbonate anion [reaction (8)], which is the first member of the series of hypothetical oligomeric carbonate ions of the general formula $C_nO_{2n+1}{}^{2-}$.

(7)



(8)



Assuming a linear structure-reactivity relationship, the rate constant of reaction (8) can be roughly estimated as 54 mol^{-1}·L·s^{-1} (see Supporting Information). This is in acceptable agreement with the rate constant of 114 ± 11 mol^{-1}·L·s^{-1} [9] for the overall reaction (5) describing the oxygen exchange between carbonic species. Thus, the dicarbonate anion is a likely intermediate for this process.

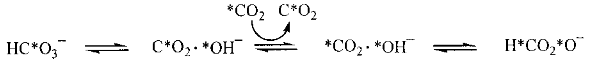
Reaction (8) has also been proposed to account for the experimental finding that the solubility of CO_2 in a ternary, eutectic melt of Li_2CO_3, Na_2CO_3 and K_2CO_3 is 50 times higher than deduced from the electrochemical reduction of "free" CO_2.[12] In a theoretical investigation of the structure and stability of the dicarbonate ion at the HF MP2 and QCISD levels a remarkably high free enthalpy of reaction for process (8) in the gas phase could be derived (ΔG = −44 to −48 kcal·mol^{-1} at 298 K).[13] If, in aqueous solution, reaction (8) was similarly exergonic, the hydrolysis of CO_3^{2-} followed by reaction (8) should result in almost complete conversion of carbonate into dicarbonate according to the overall reaction (9).

(9) $2\,CO_3^{2-} + H_2O \rightleftharpoons C_2O_5^{2-} + 2\,OH^-$

However, because of solvation effects in aqueous solution the free enthalpies of the left-hand side and the right-hand side of reaction (8) are leveled. The free enthalpies of solvation of the carbonate ion and CO_2 in water are −314[14] and −4 kcal·mol^{-1},[15] respectively. The solvation effect for the $C_2O_5^{2-}$ ion in water can be estimated, on the basis of an electrostatic model,[14] as $\Delta G_{\text{hyd.}} \approx -220$ kcal·mol^{-1}. An ionic radius, $r(C_2O_5^{2-})$, of 0.326 nm derived from the geometry-optimized structure[13] has been assumed for this purpose. From this it follows that, in water, reaction (8) is no longer exergonic and only small stationary concentrations of the dicarbonate ion are built up in a reversible reaction.

As briefly addressed in the introductory section a molecular complex between CO_2 and OH^- [7] and oligomeric cyclic orthocarbonates[8] have been discussed in the earlier literature as intermediates to explain the oxygen transfer between carbonic species. This hypothetical molecular complex is supposed to be able to exchange its CO_2 very rapidly with surrounding CO_2. This could offer an alternative rationalization for intermolecular oxygen transfer [reaction (10)].

(10)



$HC^*O_3^- \rightleftharpoons C^*O_2\cdot{}^*OH^- \overset{{}^*CO_2\ \ C^*O_2}{\rightleftharpoons} {}^*CO_2\cdot{}^*OH^- \rightleftharpoons H^*CO_2{}^*O^-$

The suggested linear arrangement of the carbon and oxygen atoms[7] to describe the molecular complex is problematic. A hydrogen-bonded structure, which is essentially a hydroxide ion solvated by carbon dioxide, would be a representation in better agreement with structural theory. However, it is difficult to see how this mode of solvation can compete with the very strong hydration of OH^- in aqueous solution. Thus, it seems unlikely that a species like $CO_2\cdot OH^-$ can exist in water with a sufficiently long lifetime to react with CO_2 present in very low concentration.

The involvement of intermediate cyclic oligomeric orthocarbonates as species responsible for oxygen exchange between the carbonic species of a carbonate solution would require the formation of new C−O bonds between carbonate and/or hydrogencarbonate units. This is rather unlikely due to the low carbonyl activity of these ions. Indeed, the negatively charged oxygen atoms of carbonate coordinate with the proton of hydrogencarbonate rather than with the much less electrophilic carbon atom. The resulting hydrogen-bridged dimeric anion $[H(CO_3)_2]^{3-}$ is well known as a structural unit in the mineral trona.[16] Higher oligomeric hydrogen-bridged carbonates of the general formula $[H_{n-1}(CO_3)_n]^{(n+1)-}$ are also known.[17,18] Of course, in this type of oligomeric carbonate oxygen transfer from carbon to carbon is not possible.

In summary, both, the involvement of a molecular complex $CO_2\cdot OH^-$ and the intermediate formation of cyclic oligomeric orthocarbonates as rationalization of the observed oxygen transfer between carbonic species in aqueous carbonate solution can be excluded. However, the reversible formation of the dicarbonate anion $C_2O_5^{2-}$ readily explains this process. The corresponding dicarbonic acid is unknown, although its dialkyl esters are well characterized and are widely used as reagents in synthetic chemistry.[19]

Experimental Section

General Remarks: The ^{13}C NMR spectroscopic data were obtained with a Bruker AMX 600 spectrometer by single-pulse excitation without proton decoupling (flip angle 30°, delay time 10 s, acquisition time 5 s). During the intervals between the measurements of the crossover experiment the tightly closed NMR tube was stored at 20 ± 0.5 °C. Sodium [^{13}C]carbonate (99% ^{13}C) was purchased from Aldrich. [^{18}O]Water recycled from ^{18}F production in the PET center, University Hospital, Tübingen, with an ^{18}O enrichment of 80% was used in the synthesis of ^{18}O-labeled sodium carbonate.

Sodium [^{18}O]Carbonate: The ^{18}O-labeled carbonate was prepared according to the method of Hutchinson and Mabuni[20] for the synthesis of sodium [^{18}O]acetate. A rigorously dried flask equipped with a septum was charged with tetraethyl orthocarbonate (5 mL, 23.8 mmol) and dehydrated 4-toluenesulfonic acid (1−2 mg). [^{18}O]Water (200 μL, 9.1 mmol, 80% ^{18}O) was then injected under magnetic stirring. After a few minutes of exothermic reaction, the mixture became homogeneous. A 0.5 M solution of sodium methoxide in dry methanol (30 mL, 15 mmol) and [^{18}O]water (350 μL, 15.9 mmol) was added to the resulting ^{18}O-labeled ethyl carbonate and the mixture heated to 70−75 °C for 30 h. A white crystalline mass precipitated. The reaction mixture was dried first in a rotary evaporator (70 °C/30 Torr) and then with an oil pump (160 °C/10^{-3} Torr); yield 1 g (98%). The degree of ^{18}O-enrichment was determined by ^{13}C NMR spectroscopy of a 0.5 M solution in D_2O containing 1 equiv. of NaOD to suppress oxygen exchange with the solvent D_2O. Four equidistantly separated signals ($\Delta\delta$ = 0.016 ppm) could be detected for the carbonate ion in an intensity ratio of 46:41:12:1 caused by $^{18}O_3$, $^{18}O_2{}^{16}O$, $^{18}O^{16}O_2$ and $^{16}O_3$ species.

Measurements of the dependence of the isotopic effect on the ^{13}C chemical shift of aqueous sodium carbonate are given in the Supporting Information. In addition to Figures 2 and 3 of the main text the full set of time-dependent intensity distributions of the $^{13}C^{16}O_{3-n}{}^{18}O_n{}^{2-}$ ions (n = 0−3) are presented as schematic diagrams. The rate constant for the addition of $CO_3{}^{2-}$ to CO_2 is estimated based on a linear relation between log k and pK_a.

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