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Carbonic Acid: Synthesis by Protonation of Bicarbonate and FTIR Spectroscopic Characterization via a New Cryogenic Technique

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Abstract: Layers of glassy solutions of HCO_3^- (DCO_3^-) and of excess HCl (DCl) dissolved in CH_3OH (CH_3OD) were deposited one by one onto each other at 78 K in the form of droplets, and their reaction has been studied *in vacuo* by FTIR spectroscopy from 78 to 300 K. At ≈120 K, i.e. ≈20 K above the solvents' glass transition temperature of 103 K, a decrease in the solvents' viscosity led to the beginning of the coalescence of the droplets. At ≈140 to ≈160 K, a further decrease in the solvents' viscosity enabled the reaction of HCO_3^- (DCO_3^-) with H^+ (D^+) as seen most clearly by the disappearance of the bicarbonate band at ≈1630 cm^{-1}. Simultaneously formation of a band centered at ≈1730 cm^{-1} (≈1725 cm^{-1}) is observed which is in the frequency region expected for a C=O stretching vibration of H_2CO_3 (D_2CO_3). Separation of the reaction product from the solvent was achieved by heating *in vacuo* up to ≈175 K and pumping off first methanol and excess HCl and then residual water. On further heating to ≈190 K, the reaction product also started to vaporize. We conclude that we have isolated carbonic acid via a novel cryogenic technique and give a preliminary assignment. It is important to note that the reaction can be reversed in an additional step by depositing a layer of KOH in glassy CH_3OH onto the isolated carbonic acid. The new cryogenic technique is particularly suitable for studies of short-lived intermediates in the reaction of nonvolatile reactants such as biomolecules. It is possibly best applied to studies of consecutive reactions where a metastable intermediate is formed in the first step in a preliminary equilibrium and the second step is rate determining.

Introduction

Carbonic acid (H_2CO_3), the short-lived intermediate in CO_2–HCO_3^-/CO_3^{2-} proton transfer reactions, is a key compound in biological and geochemical carbonate-containing systems.[1–4] It has not been isolated in its pure state or spectroscopically characterized. The literature contains reports on an ether adduct,[5,6] on its formation during thermolysis of $(NH_4)HCO_3$[7] and in proton-irradiated CO_2/H_2O ice mixtures,[8] and on NMR spectroscopic evidence for its formation in methanolic solution,[9] in addition to many kinetic[4] and computational studies.[2]

At ambient temperature H_2CO_3 dissolved in water dissociates rapidly into CO_2 and H_2O, with a rate constant of ≈20 s^{-1} and an activation enthalpy of ≈70 kJ mol^{-1} (reviewed in ref 4). Therefore, we have developed a new cryogenic technique for its isolation: Solutions of the two reactants $KHCO_3$ (or Cs_2CO_3) and HCl were quenched one by one onto each other into their glassy states on a cryoplate cooled to 78 K. Below the glass transition temperature, or T_g, of the solvent long-range diffusion and reaction is inhibited. With increasing temperatures above the solvent's T_g, the viscosity decreases sufficiently to allow diffusion and reaction of the two solutes. We chose methanol as solvent first because it can be quenched easily into the glassy state, has a low T_g of ≈103 K, and remains fluid on heating above its T_g,[10] and second because it is a sufficiently good solvent for the two reactants, and third because of its volatility.

The synthesis of H_2CO_3 was chosen to demonstrate the usefulness of the technique, but there are many other short-lived intermediates where this approach can be useful for their isolation. It is obviously not limited to methanol as solvent. Studies of short-lived intermediates at cryogenic temperatures by matrix isolation are routine and require vaporizable reactants.[11,12] But to our knowledge our approach has not been reported so far. It is particularly suitable for nonvolatile reactants such as salts which cannot be vaporized without decomposition, or even biomolecules. It is important to note that it is not limited to the reaction of two reactants but can be extended further to multi-step synthesis by adding further reactants in the form of layers of their glassy solutions as will be shown below.

Experimental Section

The glassy solutions were prepared by so-called "hyperquenching" of aerosols on a BaF_2 or CsI window held at 78 K.[13,14] This quenching technique was developed originally for vitrification of bulk water and was used here only for convenience. Other cooling methods with much lower cooling rates are also suitable for vitrification of methanol and its solutions.[10] First, droplets of a ≈0.1 M solution of $KHCO_3$ (or Cs_2CO_3) in CH_3OH made by means of a pneumatic nebulizer were suspended in N_2 gas and allowed to enter a high-vacuum cryostat through a 400 μm diameter aperture. Once inside, the droplets moved toward the cryoplate at supersonic speed and were deposited on it. The spectrum of the deposit was recorded and thereafter the procedure was repeated and a second layer of ≈1 M HCl dissolved in CH_3OH was deposited and the spectrum

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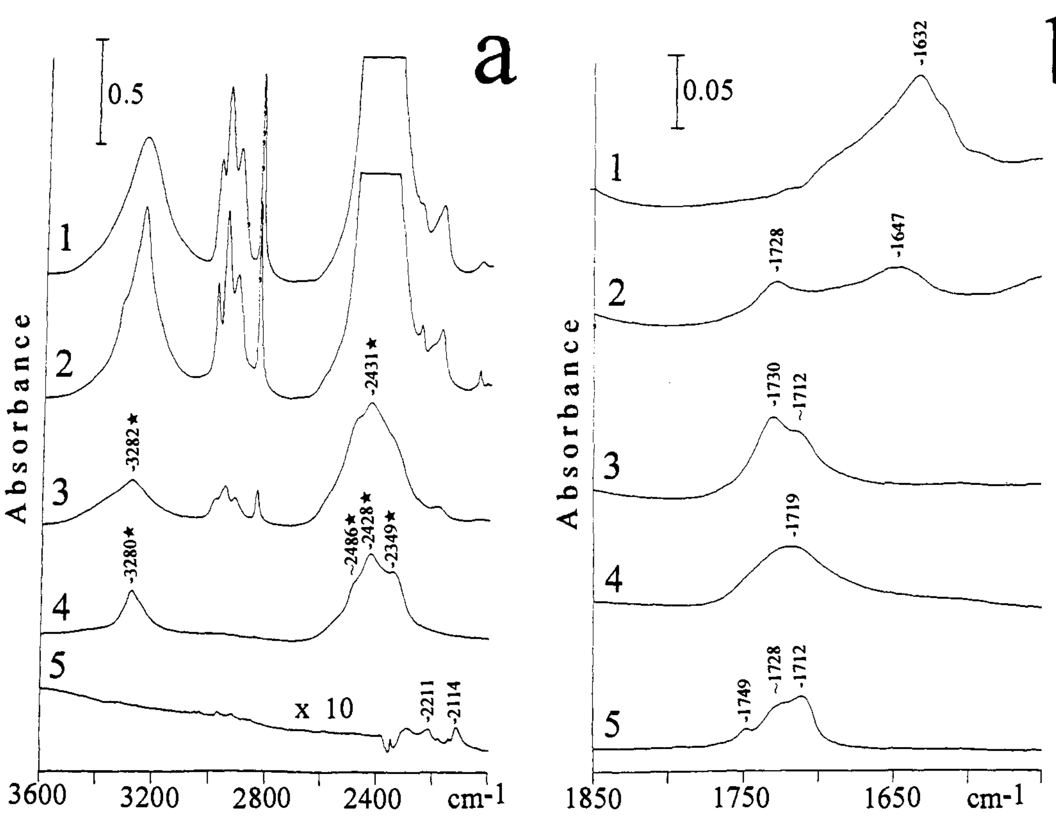

Figure 1. FTIR spectra from (a) 3600 to 2000 cm^{-1} and (b) 1850 to 1550 cm^{-1} of the reaction of a glassy solution of $KDCO_3$ dissolved in CH_3OD with DCl in CH_3OD. Curves 1 were recorded *in vacuo* at 78 K and curves 2–5 at 150, 160, 160, and 180 K, respectively. Both sets of curves are drawn on the same scale but are shifted vertically by a constant amount for clarity. Only curve 5a is shown enlarged 10-fold. The ordinate scales are given in the figure. Asterisks denote peaks due to crystalline ice.[18]

recorded again. The intensity of each deposit was chosen to be ≈0.5 absorbance units for the methanol band at 2835 cm^{-1}. Temperature was controlled with a Paar (TTK-HC) temperature controller and was constant to ±0.1 K. For additional experimental details see refs 13 and 14.

$KHCO_3$ (Riedel-de-Haen, p.a.) and Cs_2CO_3 (Merck, extra pure) were used as received. $KDCO_3$ was made from $KHCO_3$ with excess D_2O. CH_3OH (Aldrich, HPLC quality), CH_3OD (Aldrich, 99.5 atom % D), DCl (Merck, ca. 37% DCl in D_2O, >99 atom % D), and D_2O (Fluka, >99.8 atom % D) were used. $KHCO_3$ dissolved as a 0.1 M solution only after the solution was stirred for ≈24 h, whereas Cs_2CO_3 dissolved much more quickly. HCl (≈1 M solution) in CH_3OH was made with gaseous HCl, whereas the solution of DCl in CH_3OD was made by diluting the ≈12 M solution of DCl in D_2O.

The FTIR spectra were recorded in transmission on Biorad's FTS 45 at 2 cm^{-1} resolution (UDR1) by coadding 256 scans. The spectrum of water vapor was subtracted from all spectra, but no other spectral manipulations were carried out. Identical spectra were obtained with CsI or BaF_2 as window materials.

Results

The C=O stretching vibration of carbonic acid is expected at >1700 cm^{-1} and therefore its formation is followed best by development of a band in this spectral region.[8,15] In a glassy solution of HCl in CH_3OH an intense broad band partly obscures this region whereas in solutions of DCl in CH_3OD no intense spectral features were observable between 1700 and 1850 cm^{-1}. Therefore we show first the reaction of deuterated compounds and second that of the undeuterated compounds. The deposits contained some water, partly because the DCl solution was made by diluting 12 M DCl dissolved in D_2O and partly because with our experimental setup so far it is impossible to avoid leakage of air into the apparatus during quenching of the droplets. This leads to condensation of some water vapor on the quenched droplets.[14]

Figure 1 shows the spectroscopically distinct features of the reaction of $KDCO_3$ with DCl, both dissolved in CH_3OD and deposited one by one onto each other at 78 K on a CsI window. The OH and OD stretching band region is shown from 3600 to 2000 cm^{-1} (part a, Figure 1) and the CO stretching band region from 1850 to 1550 cm^{-1} (part b, Figure 1). Curves 1 were recorded at 78 K and are the spectra of the separate layers of the two reactants in glassy CH_3OD solution. The band centered at 1632 cm^{-1} is the antisymmetric stretching vibration of DCO_3^- (υ_{as}-(CO_2)),[16] broad bands centered at ≈2430 and 3280 cm^{-1} are due to OD and OH stretching vibrations of methanol and residual water, and the set of sharp bands between 2835 and 2985 cm^{-1} are due to the solvent's CH stretching vibrations.[17] Note that the spectral region >1700 cm^{-1} contains no intense spectral features.

We had previously reported that IR spectra of hyperquenched water droplets display an intense Christiansen effect in the OH (OD) stretching band region.[13,14] This artefact was also observed in this study, but it disappeared on heating this and all other samples to ≈120 K and their transmission increased simultaneously (not shown). This indicates coalescence of the droplets beginning ca. 20 deg above the solvent's T_g.

Curves 2 in Figure 1b recorded at 150 K show development of a band centered at ≈1728 cm^{-1} and decreasing intensity of the band due to DCO_3^- (part b, Figure 1). Since the intensity of the solvent's C–H stretching bands had decreased only by a few percent in going from 78 K (curve 1) to 150 K (curve 2), we conclude that reaction must have occurred in the liquid phase. In curves 3 recorded at 160 K the DCO_3^- band has disappeared and an intense band centered at 1730 cm^{-1}, with a shoulder at ≈1712 cm^{-1}, has developed (part b, Figure 1), and the intensity of the OD, OH, and CH stretching vibrations has decreased drastically (part a, Figure 1). Curves 4, which were recorded

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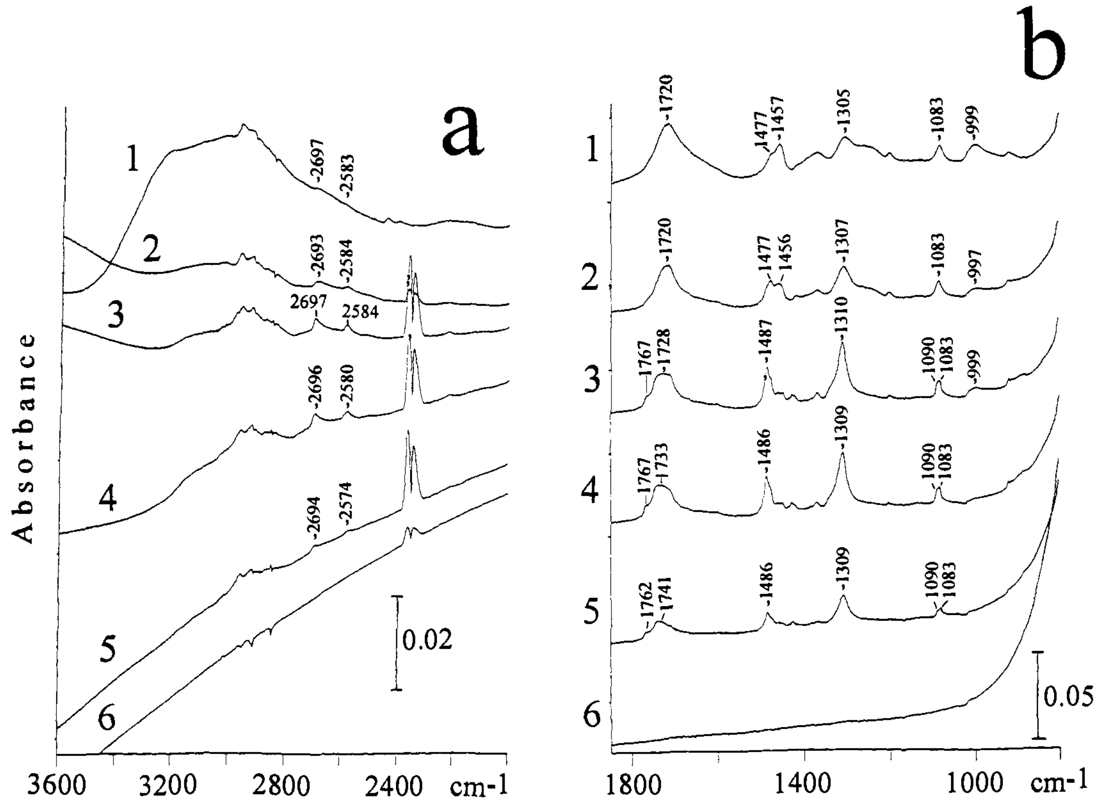

Figure 2. FTIR spectra from (a) 3600 to 2000 cm^{-1} and (b) 1850 to 800 cm^{-1} of the reaction of a glassy solution of $KHCO_3$ in CH_3OH with that of HCl in CH_3OH. Curves 1 were recorded at 190 K *in vacuo*, after pumping off the solvent. Curves 2–6 were recorded at 200, 200, 220, 240, and 300 K, respectively, at ca. 800 mbar base pressure of Ar. Both sets of curves are drawn on the same scale but are shifted vertically by a constant amount for clarity. The ordinate scales are given in the figure.

subsequently at 160 K after 25 min, show by the absence of the CH stretching vibrations that methanol has been pumped off nearly completely (part a, Figure 1), and the band maximum has shifted to ≈1719 cm^{-1} (part b, Figure 1). In curves 5 recorded at 180 K the intensity of the bands due to OD and OH stretching vibrations has decreased drastically (part 1, Figure 1, enlarged 10-fold), but the overall intensity of the band at >1700 cm^{-1} is unchanged and only becomes more structured. On further heating *in vacuo* the intensity of this band and of several other bands at lower frequency not shown in this figure decreased gradually with increasing temperature until the bands had disappeared at ≈230 K.

In curves 3 and 4, bands in the OD (OH) stretching band region marked with an asterisk are from D_2O (HOD) ice.[18] In curves 5, weak bands in the CH stretching band region are from pumping oil impurity and the weak doublet at ≈2350 cm^{-1} is from uncompensated gaseous CO_2. The quantitative removal of methanol was judged in this and the other experiments by its intense band at ≈1020 cm^{-1} (CO stretch, not shown) and its CH stretching bands.[17] According to both criteria methanol has been pumped off completely from the sample at 180 K (curves 5). In curve 5a (Figure 1) two weak bands at 2211 and 2114 cm^{-1} must belong to the same species giving rise to the structured band at >1700 cm^{-1} because their intensities decrease on further heating at the same rate.

In a second experiment, with Cs_2CO_3 instead of $KDCO_3$ as reactant, the sample was heated more slowly and kept at each temperature for ≈1 h. The beginning formation of a band at ≈1730 cm^{-1} was observed already at 140 K, and the protonation was completed at 150 K.

Figure 2 shows the spectral features of the reaction of $KHCO_3$ with HCl, both dissolved in CH_3OH and deposited on a BaF_2 window, from 3600 to 2000 cm^{-1} (part a, Figure 2) and from 1850 to 800 cm^{-1} (part b, Figure 2). In this figure we omit the first stages of the reaction shown in Figure 1 and show as curves 1 the spectrum recorded at 190 K *in vacuo*, that is after pumping off CH_3OH, excess HCl, and water to a large extent. A broad peak in the OH stretching band region (curve 1a) indicates that the sample must still contain some water. However, this band does not have the shape characteristic for H_2O ice.[18] This water was removed at the same temperature by prolonged pumping, and the apparatus was thereafter filled with ≈800 mbar of Ar in order to retard evaporation and/or decomposition of the sample. Curves 2–6 were recorded at 200, 200, 220, 240, and 300 K, respectively. Note the strongly decreasing intensity of the broad band in the OH stretching band region in curves 2–5 in part a of Figure 2. The changing slope is probably caused by the spectrometer's instability in base line. Several weak peaks between 2850 and 3000 cm^{-1} are again impurity bands from pumping oil, and the intense doublet band at 2350 cm^{-1} is due to uncompensated gaseous CO_2. The intensity of two weak bands at 2694 and 2574 cm^{-1} (curve 5, Figure 2), decreases on further heating at the same rate as those at lower frequency and must therefore belong to the same species.

In the low-frequency region (part b, Figure 2), a broad band centered at 1720 cm^{-1} in curve 1 sharpens in curve 2 and shifts to higher frequency and develops a shoulder in curves 3–5. We attribute sharpening of this band in going from curve 1 to 2 to further removal of water, as seen in part a (Figure 2), whose deformation mode is expected to contribute to its width. Sharpening of bands and splitting into several components with increasing temperature is apparent for several other band regions. It is important to note that in curves 3–5 the relative intensity of the bands decreases with increasing temperature at the same rate except for the bands at ≈1457 and ca. 999 cm^{-1}. Their intensity decreases further upon warming to 250 K (not shown) and approaches zero in curves 6 recorded at 300 K. This is strong

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evidence that the spectrum is that of a single compound and that nonvolatile $KHCO_3$ has reacted completely.

The intensity of the two bands at ≈1457 and ≈999 cm^{-1} decreases more rapidly in curves 1–3 than those of the other bands. We conclude that these two bands do not belong to the species giving rise to the other bands. We assign the band at ≈1457 cm^{-1} to the deformation mode of solvated water because its intensity decreases in curves 1–3 at a similar rate as the intensity of the broad peak centered at ≈3000 cm^{-1}. The peak at ≈999 cm^{-1} must be due to traces of solvated methanol whose CO stretching vibration is shifted to lower frequency.

The product of the reaction of $KHCO_3$ with HCl whose spectrum is shown in Figure 2 can be made to react further in a second step. In particular, we found that the reaction can be reversed by stopping at ≈180 K, cooling from 180 to 80 K, depositing a layer of droplets of a solution of KOH in CH_3OH, and rewarming in steps. We observed that reaction was reversed in the same temperature region of ≈150 to ≈160 K by disappearance of the peak at >1700 cm^{-1} and formation of the peak at ≈1630 cm^{-1}.

We have also investigated the thermolysis of NH_4HCO_3 by FTIR spectroscopy, following the procedure described in ref 7 as a convenient route to H_2CO_3, but have not been able to observe any of the intense bands shown in Figure 2.

Assignment

Before attempting assignment of the bands to H_2CO_3 (D_2CO_3), we want to emphasize the following:

(i) The reaction product is not a CH_3OH (CH_3OD) adduct. Quantitative removal of methanol was judged by its intense bands in the CH and CO stretching band region. These solvent bands are easy to distinguish from those of the reaction product because they shift only slightly upon solvation. This is in line with reports on their insensitivity to the presence of water[19] or electrolytes.[20] (ii) It is not simply a mixture of CO_2 and H_2O formed by decomposition of H_2CO_3 (see Figure 1 of ref 8 for an IR spectrum of a CO_2/H_2O ice mixture). (iii) The spectrum is clearly different from that of the residual film formed after proton irradiation of CO_2/H_2O ice mixtures which has been tentatively assigned as H_2CO_3.[8] (iv) It is not a sesquicarbonate ion, formed by hydrogen bonding of H_2CO_3 with HCO_3^- and postulated as an intermediate,[21] because the excess of HCl used in these studies and the absence of a nonvolatile residue proves that bicarbonate has been protonated quantitatively. After having ruled out these possibilities, we attempt in the following a preliminary assignment of the major features.

The assignment of the spectral features of H_2CO_3 (D_2CO_3) is complicated, first, because we do not know its structure. Ab initio SCF calculations have shown that for isolated H_2CO_3 the trans-trans structure is the most stable conformation, although the cis-trans conformer is only ca. 4 kJ mol^{-1} higher in energy.[2] For the solid, or crystalline, state we expect in addition strong intermolecular hydrogen bonding. For crystalline formic and acetic acid, the hydrogen-bonded chain structure in the crystal led to further complications in the assignment of their vibrational spectra.[22-24] For example, Millikan and Pitzer[22] attributed the crystal splitting of ≈100 cm^{-1} of the C=O stretching vibration in crystalline formic acid to the presence of strong H bonds in the crystal. Intermolecular H bonding is also expected for carbonic acid in its solid state. Second, the comparatively intense O–H stretching band in the spectrum of D_2CO_3 indicates a considerable amount of $HDCO_3$ (see Figure 1a, curve 4). And third, we can, after removal of methanol, differentiate in a simplifying way three spectroscopically different states for the reaction product which are the following: (i) 180–190 K, carbonic acid in the presence of excess water and ice (note in curves 4 of Figure 1 and curves 1 of Figure 2 the comparatively intense OH (OD) stretching band (part a) and the widths of the bands due to carbonic acid (part b)); (ii) ≈200 K, in curves 2 of Figure 2 the decreased intensity in the OH stretching band region (part a) and unstructured but sharpened bands at e.g. ≈1720 cm^{-1} are suggestive of H_2CO_3 in an amorphous form; and (iii) ≥200 K, splitting and further sharpening of bands observable in curves 3–5 of Figure 2 is suggestive of crystallization of H_2CO_3. Therefore, it is important to compare the same spectral states of H_2CO_3 and D_2CO_3, and we use in the following state (iii) for assignment (i.e. for H_2CO_3 curves 3–5 of Figure 2, and for D_2CO_3 curves 5 in Figure 1), because our assignment is based on comparison with spectroscopic studies of crystalline carboxylic acids[22,23] and of crystalline bicarbonate salts.[16,24-26]

The structured C=O stretching band shifts very little upon deuteration, namely from ≈1730 cm^{-1} for its peak maximum to ≈1712 cm^{-1}: this rules out assignment of this band to a OH deformation mode. The symmetric stretching vibration of the $C(OH)_2$ ($C(OD)_2$) group of carbonic acid is assigned to a band at 1083 (1064) cm^{-1}. Complications arise in assignment of the antisymmetric stretching vibration because for H_2CO_3 *two* intense bands are present at ≈1486 and 1309 cm^{-1}. For D_2CO_3, two structured bands of similar intensity are observed centered at ≈1466 and ≈1368 cm^{-1} (not shown). Therefore, we have two sets of bands, namely at 1486 and 1466 cm^{-1} on the one hand and at 1309 and 1368 cm^{-1} on the other, which are both in the region characteristic for the antisymmetric stretching motion. For the first pair of bands, decrease in frequency upon deuteration is as expected for an antisymmetric $C(OH)_2$ stretching vibration. But for the second pair of bands, the frequency increases upon deuteration, namely from 1309 to 1368 cm^{-1}. We note that similar behavior was also observed by others and attributed to vibrational coupling of the in-plane C–O–H bending motion with C–O stretching motions.[22,25] We therefore tentatively suggest that solid carbonic acid is present either as a mixture of two conformers and/or that intermolecular hydrogen bonding leads to two spectroscopically different states.

The two weak bands at ≈2694 and ≈2580 cm^{-1} (2211 and 2114 cm^{-1}) are assigned as O–H (O–D) stretching vibrations. The two sets of bands cannot be easily assigned to an overtone or a combination band, and both sets decrease in intensity on further heating at a similar rate as the other bands at lower frequency. Their isotopic ratio of 1.22 is low, but we note that ratios of 1.27 have been reported for the bicarbonate ion,[25] and even similar average O–H and O–D stretching frequencies were reported for systems with strong hydrogen bonding.[27] Frequencies and their preliminary assignment are listed in Table I.

Discussion

The temperature dependence of viscosity of a glass is used to advantage in this cryogenic technique, and we can differentiate between the following temperature regions: (1) At $T < T_g$, long-range diffusion is inhibited. Therefore even deposits of glassy solutions of two highly reactive reactants such as HCl and HCO_3^- can be studied at leisure without occurrence of their reaction. (ii) At ≈120 K, i.e. ≈20 K above the T_g of 103 K for the solvent,[10] viscosity of the solvent has decreased sufficiently to enable coalescence of the quenched droplets to an extent that the

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Table I. Infrared Frequencies[a] (cm^{-1}) due to H_2CO_3 and D_2CO_3 and Their Preliminary Assignment

H_2CO_3	D_2CO_3	assignment
2694, vw	2211, vw	O–H (O–D) str
2580, vw	2114, vw	
1730, st	1712, st	C=O str
1486, st	1466, st	$C(OH)_2$, $C(OD)_2$ antisym stretching vibrations?
1309, st	1368, st	
1083, *m*	1064, *m*	$C(OH)_2$ *sym* str

[a] Frequencies for H_2CO_3 are from curves 3 to 5 of Figure 2 and for D_2CO_3 in part from curves 5 of Figure 1. vw = very weak, m = medium, st = strong.

Christiansen effect disappeared and transmission of the sample increased. But, viscosity of the droplets is still too high to enable diffusion of the solutes and their reaction. (iii) At ≈140 to ≈160 K, i.e. ≈40 to ≈60 K above T_g, viscosity has decreased even further such that quantitative reaction of the two reactants occurs. It is important to note that these temperatures are for the time scale of our experiment which is ≈1 h for each temperature step. The above discussion is based on the reported T_g of 103 K for methanol,[10] but we expect very little change of this value for its dilute solutions or for the monodeuterated solvent.

An estimate for the viscosity, η, at these temperature regions is obtainable by the Williams et al.[28] empirical relationship for the temperature dependence of η between T_g and (T_g + ≈50 K) (read from their Figure 2). At T_g, η is generally considered to be $\approx 10^{12}$ Pa s. At ≈20 K above T_g, η decreases to $\approx 10^7$ Pa s. At ≈40 to ≈60 K above T_g, η decreases further from $\approx 10^4$ to $\approx 10^2$ Pa s. These estimates hold for glass-forming organic, inorganic, and polymeric liquids of widely differing T_g values. We therefore expect that for glass-forming solvents other than methanol a similar increase in temperature above their respective T_g values is necessary to induce processes ii and iii.

We do not know yet if carbonic acid prepared by reaction of bicarbonate with acid vaporizes by decomposition to CO_2 and H_2O or can be sublimed without decomposition. Molecular orbital calculations of the gas-phase dehydration of isolated H_2CO_3 gave an activation barrier of between 221 and 264 kJ mol^{-1}, depending on the chosen wave function.[29] Therefore, it is conceivable that solid carbonic acid can be vaporized without decomposition. The mass-spectral characterization of H_2CO_3 formed by thermolysis of $(NH_4)HCO_3$ is further support for its stability in the gas phase.[7]

It has been argued that the reaction of HCO_3^- with H^+ to CO_2 and H_2O may either follow a reaction path where HCO_3^- is protonated in a pre-equilibrium step, with carbonic acid as metastable intermediate, or proceed via a rate-determining dehydration step, and that kinetics cannot distinguish between the two mechanisms.[3,30] The apparently successful isolation of carbonic acid reported in this study is strong evidence for the former mechanism. We note that Olah and co-workers recently have reported NMR spectroscopic evidence for carbonic acid formed at low temperatures in methanolic solution.[9]

We conclude that this novel cryogenic technique is probably best applied to studies of consecutive reactions where a metastable intermediate is formed in a first step in a preliminary equilibrium, and where a second much slower step is rate determining. Vitrification of solutions of two reactants on top of one another does not necessarily require "hyperquenching" of aerosol droplets which was used in this study for convenience. For example, methanol and its solutions can be vitrified already by quenching the sample in liquid nitrogen,[10] and an alternative and much more simpler method is to spray with a retouching air brush solutions of two reactants one by one on a suitable cryoplate held at a temperature below the T_g of the solvent. Investigation of a reaction product is obviously not restricted to FTIR spectroscopy, and we have started to study the applicability of other spectroscopic and diffraction techniques and to upscale the reaction.

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