

Tracing the Acetalization of Cyclohexanone in CO₂-Expanded Alcohols by Attenuated Total Reflection Infrared Spectroscopy

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The CO₂-catalyzed acetalization is regarded as a promising alternative to the conventional acid-catalyzed method from a viewpoint of green chemistry (C. A. Eckert et al., *Ind. Eng. Chem. Res.* **43**, 2605 (2004)). We have applied *in situ* attenuated total reflection infrared (ATR-IR) spectroscopy for elucidating and monitoring the acetalization of cyclohexanone in CO₂-expanded ethylene glycol and methanol at 50 °C and 3 MPa. The ATR-IR spectra of the reaction mixtures periodically recorded with a ZnSe crystal demonstrate that ATR-IR spectroscopy is a practical tool for tracing the kinetics of acetalizations *in situ*. In addition, the rate of CO₂ dissolution as well as CO₂ solubility into the cyclohexanone–alcohol mixtures could be evaluated from the CO₂-v₃-antisymmetric stretching band. The ZnSe ATR crystal, however, was corroded during longer use under the acidic conditions realized by the dissolution of CO₂ in the alcohols. In contrast, the corrosion did not occur when a Ge crystal was used instead of a ZnSe crystal, and therefore the application of a Ge ATR crystal is recommended for continuous long-term experiments with these media.

Index Headings: Attenuated total reflection infrared spectroscopy; ATR-IR spectroscopy; Acetalization; CO₂-expanded alcohols; Cyclohexanone; ZnSe crystal; Ge crystal; High pressure.

INTRODUCTION

CO₂-expanded liquids (CXLs) are promising media for performing separations, extractions, and catalytic and non-catalytic reactions, as well as for other applications.¹ One of the most promising CXLs in terms of “green” chemical synthesis is the CO₂-expanded alcohol, which exhibits acidity and thus can promote acid-catalyzed reactions. It is well known that water, when it dissolves CO₂, shows acidity owing to the formation of carbonic acid (HOC(O)OH). By analogy, alkylcarbonic acid, ROC(O)OH, is considered to form in CO₂-expanded alcohols (ROH), creating acidic environments. Eckert’s group used diazodiphenylmethane as a probe molecule to trap the acidic species generated in CO₂-expanded alcohols.^{2,3} They showed that the alcohol–CO₂ complexes react similarly to carboxylic acids with the probe molecule, indicating the formation of alkylcarbonic acids in CO₂-expanded alcohols. More recently, they developed a technique to measure the alkylcarbonic acid formations and the dissociation constants in CO₂-expanded methanol, ethanol, and benzyl alcohol at 25 °C.⁴

The utility of CO₂-expanded alcohols not only as solvents but also as acid catalysts was first demonstrated by Eckert and co-workers. They reported that the acetalization of cyclohexanone with methanol is accelerated remarkably in the presence of CO₂ (Scheme 1); under optimal conditions, the rate in CO₂-expanded methanol was 130 times faster than that in CO₂-free methanol.^{5–7} They also found that the hydrolysis of β-pinene to

terpineol and other alcohols proceeds in CO₂-expanded 1:1 MeOH–H₂O mixture, whereas the same reaction did not take place in the absence of CO₂.^{6–8} The diazotization of aniline and subsequent coupling to give methyl yellow or substitution to give benzyl iodide was also shown to be accelerated in CO₂-expanded methanol.⁹ Another successful example of the use of CO₂-expanded alcohols in organic synthesis is the Ugi reaction, which involves the addition of alkylcarbonic acid to the intermediate nitrilium ion.¹⁰ These examples clearly emphasize not only the high utility of CO₂-expanded alcohols for acid-catalyzed reactions, but also the potential of the CXLs as alternatives to conventional, problematic acid catalysts used in industrial processes. Disposal of solid acid catalysts or neutralization of homogeneous acid catalysts giving waste salts are still environmental issues in conventional processes, whereas the active acidic species, alkylcarbonic acids, in CO₂-expanded alcohols can easily be decomposed to alcohols and CO₂ just by depressurization of CO₂.

One technical problem of the reactions in CO₂-expanded alcohols arises from the high-pressure CO₂ conditions, which require a tightly closed stainless-steel reactor. The composition of reaction mixtures is therefore known only when the reactor is opened through troublesome procedures including depressurization and decomposition of the cell. Hence, more facilitated methods that furnish information on the compositions are highly desired from a practical point of view.

In situ attenuated total reflection infrared (ATR-IR) spectroscopy, if the ATR crystal is placed at the bottom of the cell, is a powerful tool to investigate gas-expanded liquids.¹¹ For example, Kazarian’s group^{12–15} and our group¹⁶ have used this spectroscopy to elucidate the molecular interactions in CO₂-expanded ionic liquids. Here, we have applied ATR-IR spectroscopy to elucidate CO₂-expanded liquids composed of cyclohexanone and alcohols and have evaluated the potential and limitations of this spectroscopy for tracing the acetalizations.

EXPERIMENTAL

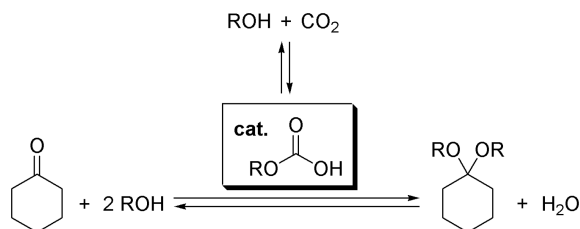
Chemicals. Liquid CO₂ (PanGas; purity 99.995%) was used as received. Commercially available high-grade cyclohexanone (Fluka; product no. 29140; ≥99.5%), methanol over molecular sieve (Fluka; product no. 65542; ≥99.5%), and anhydrous ethylene glycol (Fluka; product no. 324558; 99.8%) were used as received from the freshly opened bottles.

High-Pressure Attenuated Total Reflection Infrared Cell and Procedures. **SAFETY NOTE:** *The present experiments involve the use of relatively high pressures and require equipment with the appropriate pressure rating.* The specially constructed high-pressure cell (ETH workshop, Fig. 1) had an internal volume of 10 mL and possessed an ATR crystal (ZnSe or Ge; size 50 mm × 20 mm × 2 mm; angle of incidence 60°; Crystran Ltd.).^{16,17} The IR beam reflects six times at the

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SCHEME 1. *In situ* formed alkylcarbonic acid-catalyzed acetalization of cyclohexanone with alcohols under compressed CO_2 .

interface of the CO_2 -expanded reaction mixtures with the ATR crystal surface. Spectra were recorded with a resolution of 2 cm^{-1} using an EQUINOX-55 Fourier transform infrared (FT-IR) spectrometer equipped with a liquid- N_2 -cooled MCT detector (Bruker Optics). High-pressure liquid CO_2 was fed into the cell using a PM-101 compressor (NWA), of which pressure was set below the limitation pressure of the whole system.

In situ ATR-IR spectra during the acetalizations were recorded as follows: 0.5 mL of cyclohexanone and 5 mL of anhydrous alcohol were loaded simultaneously in the cell using two syringes under N_2 atmosphere. The cell was sealed and heated to $50\text{ }^\circ\text{C}$. Then, the compressed liquid CO_2 was introduced until the pressure reached 3 MPa. The acetalization mixtures were not stirred unless otherwise stated.

The product liquid mixtures were analyzed also by ^1H and ^{13}C nuclear magnetic resonance (NMR, Bruker Avance 500, 500 MHz), a gas chromatograph (GC, Hewlett Packard, model HP 6890) equipped with an HP-5 column (J & W Scientific, $25\text{ m} \times 0.32\text{ mm} \times 0.17\text{ }\mu\text{m}$), and a gas chromatography–mass spectroscopy (GC-MS system, Hewlett Packard) composed of an HP 6890 GC (column: HP-5MS, J & W Scientific, $25\text{ m} \times 0.2\text{ mm} \times 0.33\text{ }\mu\text{m}$) and an HP 5973 mass selective detector. The GC analyses were performed using a flame ionization detector (FID) under the following column-temperature conditions: $50\text{ }^\circ\text{C}$ (10 min) $\rightarrow 20\text{ }^\circ\text{C min}^{-1} \rightarrow 250\text{ }^\circ\text{C}$ (5 min).

Scanning Electron Microscopy. Scanning electron microscopy (SEM) was performed on a Gemini 1530 field emission microscope (Zeiss). Secondary electron images of the as-obtained samples were recorded at 1 kV.

RESULTS AND DISCUSSION

Acetalization of Cyclohexanone in CO_2 -Expanded Ethylene Glycol over ZnSe Attenuated Total Reflection Crystal. The *in situ* ATR-IR spectra recorded during the

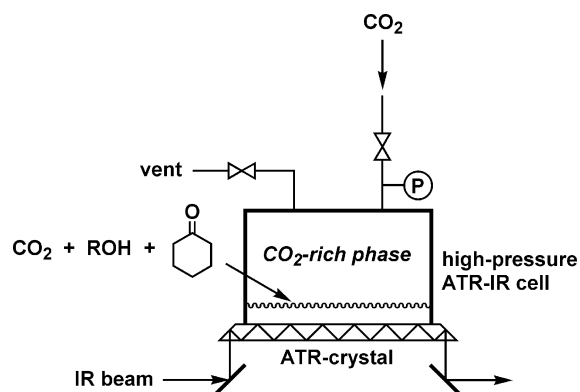


FIG. 1. ATR-IR cell used in the present research.

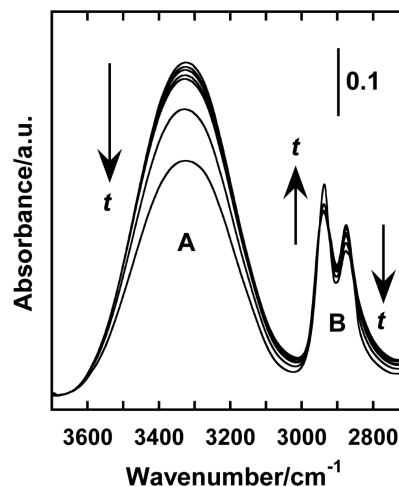


FIG. 2. Change of the ATR-IR spectrum during the acetalization of cyclohexanone in CO_2 -expanded ethylene glycol at $50\text{ }^\circ\text{C}$ and 3 MPa in (A) the O–H stretching mode region and (B) the $\text{C}(\text{sp}^3)$ –H stretching mode region. A ZnSe crystal was used. The mixture was not stirred. The spectra were recorded at 0, 1, 2, 4, 6, 8, and 10 h after the addition of CO_2 . Note the arrow sign indicating the time change.

acetalization of cyclohexanone with ethylene glycol at $50\text{ }^\circ\text{C}$ under 3 MPa CO_2 are shown in Figs. 2–5. Although ZnSe is known to react with acids to give toxic H_2Se ,¹⁸ reasonable spectra could be obtained under the acidic conditions, indicating that the acidity of this medium is not strong enough to promote the rapid decomposition/dissolution of ZnSe. Note, however, that the surface of ZnSe crystal gradually underwent corrosion, and this was accelerated by stirring of the acetalization mixture (see the Kinetic Graphs subsection below).

The formation of the corresponding five-membered cyclic acetal involves the disappearance of two OH groups in an ethylene glycol molecule, while it is accompanied by the formation of one H_2O molecule (Scheme 1). As shown in the behavior of band A in Fig. 2, the overall intensity of the OH

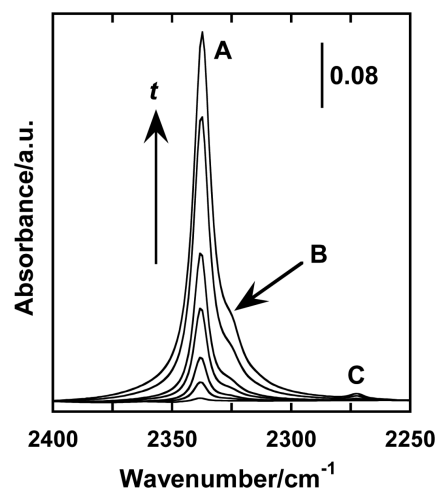


FIG. 3. Change of the ATR-IR spectrum during the acetalization of cyclohexanone in CO_2 -expanded ethylene glycol at $50\text{ }^\circ\text{C}$ and 3 MPa in (A) the CO_2 - ν_3 -antisymmetric stretching mode region with (C) the corresponding $^{13}\text{CO}_2$ band and (B) the $(\nu_3 + \nu_2) - \nu_2$ hot band. A ZnSe crystal was used. The mixture was not stirred. The spectra were recorded at 0, 1, 2, 4, 6, 8, and 10 h after the addition of CO_2 . Note the arrow sign indicating the time change.

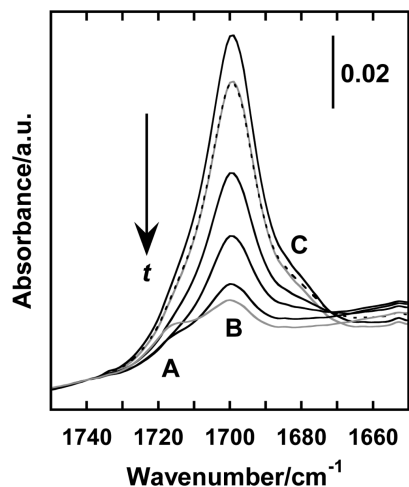


FIG. 4. Change of the ATR-IR spectrum during the acetalization of cyclohexanone in CO₂-expanded ethylene glycol at 50 °C and 3 MPa in (A, B, and C) the C=O stretching mode region. A ZnSe crystal was used. The mixture was not stirred. The spectra were recorded at 0 (gray solid line), 1, 2 (black broken line), 4, 6, 8, and 10 h (gray solid line) after the addition of CO₂. Note the arrow sign indicating the time change.

stretching mode band decreased drastically as the reaction proceeded, indicating that the intensity decrease of the ethylene glycol band prevailed over the intensity increase of the H₂O band. The top parts of the C(sp³)-H stretching mode band B slightly changed according to the increased and decreased amounts of the acetal product and the reactants (ethylene glycol and cyclohexanone), respectively.

Figure 3 shows the change of the CO₂-v₃-antisymmetric stretching mode band^{16,19,20} with time. Band C is assigned to natural ¹³CO₂, while band B is probably due to the (v₃ + v₂) -

v₂ hot band.^{21,22} Compared to the v₃ band of pure CO₂ at 50 °C and 3 MPa, which displays the P- and R-branches,²⁰ the main band A was not split and was far less intense owing to the smaller amount of dissolved CO₂. In addition, band A was much narrower, likely due to the impeded rotational motion by the interaction with ethylene glycol. It should be noted that band A increased very slowly with time, because of the sluggish rate of CO₂ dissolution in ethylene glycol. This was also confirmed by the gradual decrease of CO₂ pressure with time, which was compensated by adding further amounts of CO₂ to the cell to keep the pressure constant. Microscopically, the slow-rate dissolution of CO₂ probably originates from the strong intermolecular interactions among ethylene glycol molecules, which form a relatively strong hydrogen-bond network and cause the relatively high viscosity of ethylene glycol. The former report by Eckert and co-workers mainly focused on acetalization with methanol, and the detailed kinetics of the reaction with ethylene glycol were not given.⁵ Since the intensity of the CO₂ v₃ band increased slowly even when the acetalization mixture was stirred, the mass transfer of CO₂ also must be taken into account when the detailed kinetics of the reaction is considered.

The change of the C=O stretching mode band of cyclohexanone is shown in Fig. 4. This band change is probably most reliable for checking the extent of the progress of acetalization. Our group, for example, has shown that the intensity change of the C=O band actually can be used for making a calibration curve for quantitative analysis in the catalytic chemical fixation of CO₂ with epoxides.¹⁷ In the present experiment, the relative intensity of the C=O band just after the addition of CO₂ was lower than that at 1 h. Since the spectra were recorded under static conditions, this was probably due to a heterogeneous distribution of ethylene

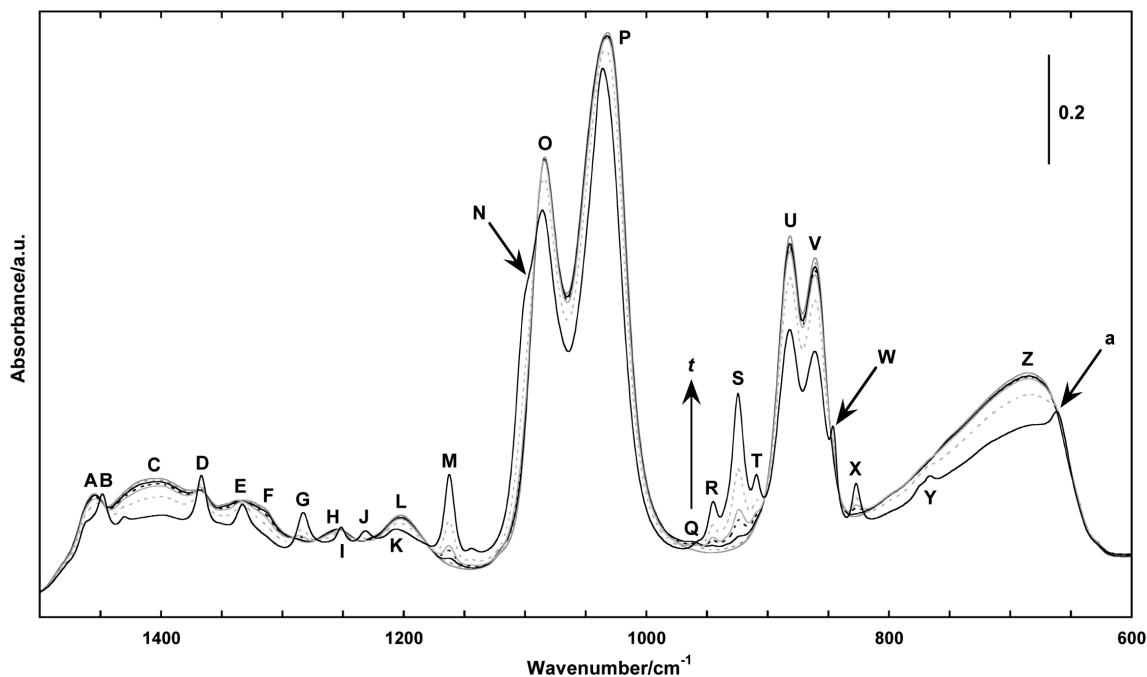


FIG. 5. Change of the ATR-IR spectrum during the acetalization of cyclohexanone in CO₂-expanded ethylene glycol at 50 °C and 3 MPa in the fingerprint region. The bands denoted with the alphabet are those showing change with time. A ZnSe crystal was used. The mixture was not stirred. The spectra were recorded at 0 (strong gray solid line), 1 (strong gray broken line), 2 (black solid line), 4 (black broken line), 6 (pale gray solid line), 8 (pale gray broken line), and 10 h (black solid line) after the addition of CO₂. Note the arrow sign indicating the time change.

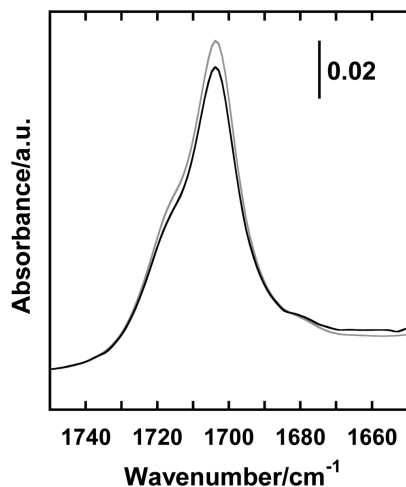


FIG. 6. Change of the ATR-IR spectrum during the acetalization of cyclohexanone in CO₂-expanded methanol at 50 °C and 3 MPa in the C=O stretching mode region. A ZnSe crystal was used. The mixture was not stirred. Gray spectrum, 10 min; black, 4.83 h.

glycol, cyclohexanone, and CO₂. However, after 1 h, the decrease of the band with time could clearly be seen, indicating the conversion of cyclohexanone to the corresponding acetal. Strictly, the C=O band was composed of three bands. At the initial stage of the reaction, an intense band B was observed at 1700 cm⁻¹ with a shoulder band C at 1685 cm⁻¹. Intriguingly, however, as the intensity of bands B and C decreased with the time, at the end of the reaction appeared another band A at a higher wavenumber of 1716 cm⁻¹. Similar C=O band discreteness was also observed by other groups for CO₂-free carbonyl compound–alcohol and carbonyl compound–water systems.^{23–25} They attributed the highest wavenumber band to a non-hydrogen-bonded free C=O bond, whereas the bands at lower wavenumbers were suggested to be due to the C=O bond hydrogen-bonding with alcohol or water. According to their assignment, band A can be attributed to the non-hydrogen-bonded C=O bond, while band B is assignable to the mono-hydrogen-bonded C=O bond. The shoulder band C is difficult to interpret. One possible assignment for this band is the C=O bond di-hydrogen-bonding with ethylene glycol. However, this still remains inconclusive, because the earlier work by Symons and Eaton revealed that not only methanol but also ethylene glycol cannot di-hydrogen-bond with acetone at 25 °C.²⁴ In addition, Saied and co-workers observed a much greater shift for the C=O bond in 3,3,5,5-tetramethylcyclohexanone doubly hydrogen-bonding with a specially designed diphenol, 2,2'-(1,2-ethynediyl)bis[6-(1,1-dimethylethyl)-4-methylphenol] (free C=O, 1717 cm⁻¹; di-hydrogen-bonded C=O, 1670 cm⁻¹).²⁶ We confirmed that band C similarly appeared even for the CO₂-free ethylene glycol–cyclohexanone mixture, and thus this band is not related to the alkylcarboxylic acids formed by the reaction between ethylene glycol and CO₂ (Scheme 1).

Figure 5 shows the band changes in the finger-print region, which shows the clear increase and decrease of the bands due to the product and reactants, respectively. The intensity decrease of the broad band Z allowed the CO₂-v₂-bending mode band a to appear at 662 cm⁻¹. This wavenumber is very close to that observed for the CO₂-expanded benzyl alcohol at 80 °C and 16 MPa,²⁷ and shifted to a lower wavenumber compared to that of pure CO₂ at 50 °C and 3 MPa (667 cm⁻¹),

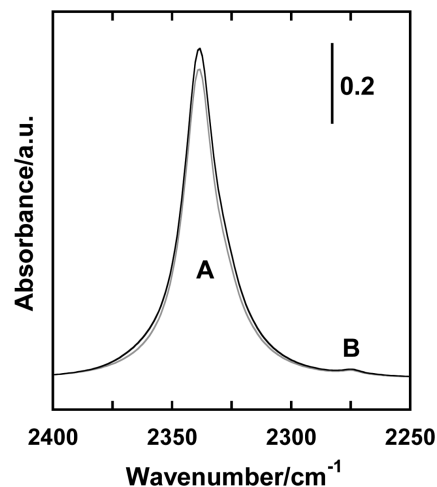
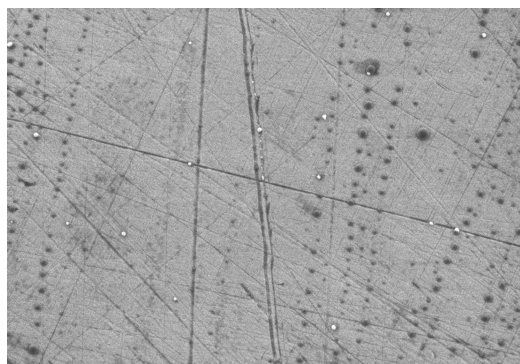


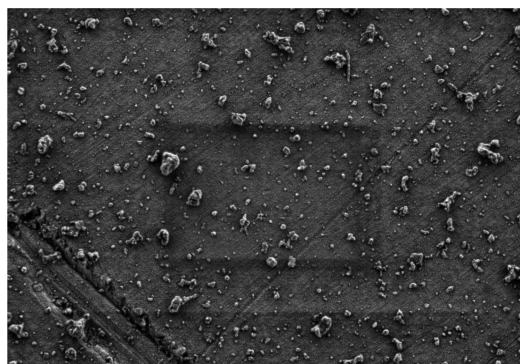
FIG. 7. Change of the ATR-IR spectrum during the acetalization of cyclohexanone in CO₂-expanded methanol at 50 °C and 3 MPa in (A) the CO₂-v₃-antisymmetric stretching mode region with (B) the corresponding ¹³CO₂ band. A ZnSe crystal was used. The mixture was not stirred. Gray spectrum, 10 min; black, 4.83 h.

indicating that the surrounding ethylene glycol molecules interacting with CO₂ suppressed the bending vibration of CO₂.

Acetalization of Cyclohexanone in CO₂-Expanded Methanol over the ZnSe Attenuated Total Reflection Crystal. *In situ* ATR-IR spectroscopy was also successfully applied for the acetalization of cyclohexanone in CO₂-expanded methanol under otherwise similar conditions, though the change of the bands was much less drastic due to the sluggish reaction. Similar increase and decrease of the bands due to the corresponding acetal and the reactants (methanol and cyclohexanone), respectively, could be observed, as, for example, shown in Fig. 6. One remarkable difference compared to the former system with ethylene glycol was that CO₂ dissolved much faster in the liquid phase composed of methanol and cyclohexanone. As shown in Fig. 7, the intensity of the CO₂ v₃ band recorded at 10 min was already very close to that at 4.83 h, although the mixture was not stirred. It also should be noted that the amount of dissolved CO₂ was much greater for the methanol–cyclohexanone–CO₂ system than for the former ethylene glycol–cyclohexanone–CO₂ system, as evidenced from the much stronger intensity of the CO₂ v₃ band. Knowing the refractive index of methanol and ethylene glycol, it is possible to estimate the mole fraction of CO₂ in the methanol–cyclohexanone–CO₂ mixture, which is approximately double the CO₂ mole fraction in the ethylene glycol–cyclohexanone–CO₂ mixture. There was also a large difference in broadness of the band between the two systems; the (v₃ + v₂) – v₂ hot band was hidden by the broad CO₂ v₃ band for the present system (Fig. 7), indicating that the rotational motion of CO₂ molecules in the CO₂-expanded methanol–cyclohexanone was not so strongly impeded as in the CO₂-expanded ethylene glycol–cyclohexanone. The much weaker strength of attractive intermolecular interactions among methanol molecules, which can also be seen in the higher volatility and lower boiling point of methanol, resulted in the faster and greater dissolution of CO₂; the vapor pressures (20 °C)/boiling points of methanol and ethylene glycol are 97.68 mmHg/64.7 °C and 0.08 mmHg/196–198 °C, respectively, according to the data published by Sigma–Aldrich.



(a)



(b)

FIG. 8. SEM images of the surface of the ZnSe crystal (a) before and (b) after having been immersed in CO₂-expanded methanol at 50 °C and 3 MPa for 6 h. The length of the pictures corresponds to 19.2 μm.

Kinetic Graphs. We have also measured the ATR-IR spectra of the methanol–cyclohexanone–CO₂ system and the ethylene glycol–cyclohexanone–CO₂ system under “stirred” conditions using the ZnSe ATR crystal. Stirring the methanol–cyclohexanone–CO₂ system accelerated the corrosion of the crystal surface; the baseline of the spectrum suddenly moved up after 4 h, and a reasonable spectrum was no longer available. The surface and probably also the subsurface of the ZnSe crystal underwent decomposition through the reaction with the acidic CO₂-expanded methanol,¹⁸ and the contact of a possible acidic species, i.e., methylcarbonic acid, with the crystal surface became more intense with stirring of the mixture. SEM images of the surface of the ZnSe crystal before and after having been immersed in the CO₂-expanded methanol at 50 °C and 3 MPa for 6 h are shown in Fig. 8. As emerges from these images, the acidity of this medium could change the clearly flat surface of the parent ZnSe crystal to an awfully rugged one. The corrosion was less prominent for the ethylene glycol–cyclohexanone–CO₂ system, which seems to be related to the smaller dissolved amount of CO₂ and to the higher viscosity of the mixture inhibiting the contact of the acidic species with the crystal surface. Until the ZnSe crystal was deteriorated, however, reasonable band-intensity changes of the reactants and products were observed, and we could successfully plot kinetic graphs for the two acetalization systems, respectively, which are shown in Fig. 9.

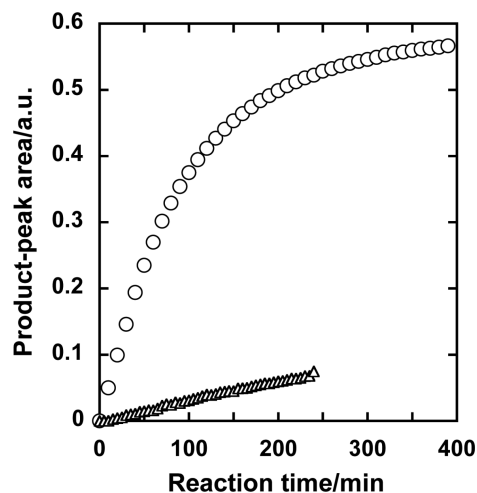


FIG. 9. Variations of the product-peak area as a function of reaction time during the acetalization of cyclohexanone in CO₂-expanded methanol (triangles) and ethylene glycol (circles) at 50 °C and 3 MPa. A ZnSe crystal was used. The mixtures were stirred. The integrations for the peak-area calculations were performed with a spectroscopic software OPUS, version 5 (Bruker Optics) in the wavenumber range 940–915 cm⁻¹, using the type-B integration method.

Further Comments. *In situ* ATR-IR spectroscopy thus has been demonstrated to be able to furnish information on the composition of CO₂-expanded acetalization mixtures, which changes with time. Since the acetalizations are performed under relatively high pressure CO₂ conditions and thus require reactors that are not easily opened, *in situ* spectroscopy will be highly demanded if the acetalizations or their related reactions are commercialized. In addition, we could also obtain some new insight into the acetalizations that was not discussed previously by Eckert and co-workers^{5–7} such as the difference in the CO₂ dissolution rate between ethylene glycol–cyclohexanone mixtures and methanol–cyclohexanone mixtures, and the discrete carbonyl bands probably indicating the presence of free cyclohexanone and mono-hydrogen-bonded cyclohexanone in the CO₂-expanded ethylene glycol–cyclohexanone.

The method, however, did not furnish the decisive mechanistic information such as the presence of alkylcarbonic acids or possible intermediates such as hemiacetals. This was probably because these “key” species existed in extremely low concentrations or their lifetimes were too short to be detected by IR spectroscopy. Even for the acetalization under conventional conditions, we are unaware of any published reports showing the spectra of possible intermediates; the well-established mechanism has been proposed based only on the results of kinetic analyses.^{28,29}

The concurrent analysis of the resultant liquid phases by ¹H/¹³C NMR, GC, and GC-MS revealed that the reactions took place in almost 100% selectivity, although, in some cases, a negligible amount of 1-methoxycyclohexene was detected for the acetalization of cyclohexanone in CO₂-expanded methanol.

Although *in situ* ATR-IR spectroscopy is thus considered to be a promising tool for tracing the acetalizations, we should note a limitation of the ZnSe crystal, namely, its sensitivity to acidic conditions. As we observed in a sudden jump up of the baseline of the spectrum after the 4-h acetalization of

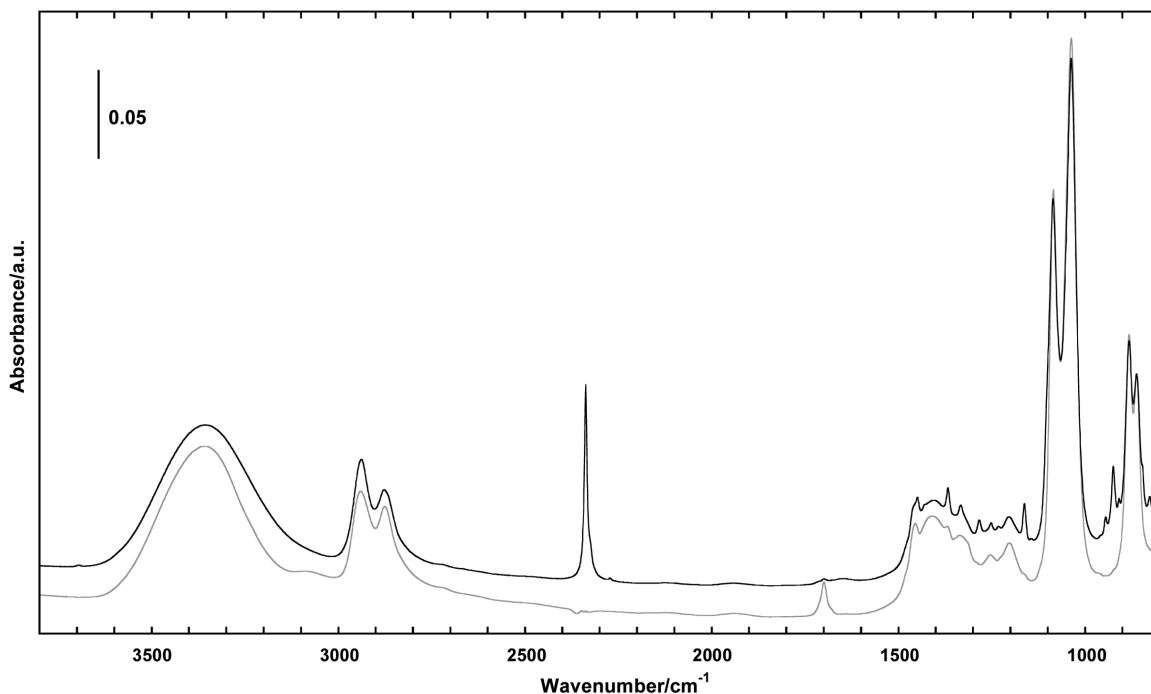


FIG. 10. Change of the ATR-IR spectrum during the acetalization of cyclohexanone in CO₂-expanded ethylene glycol at 50 °C and 3 MPa in the wavenumber range 3800–800 cm⁻¹ recorded with a Ge ATR crystal. The mixture was not stirred. The spectra were recorded at 0 (gray line) and 8 h (black line), respectively, after the addition of CO₂.

cyclohexanone in CO₂-expanded methanol, the surface of the ZnSe crystal was corroded under the acidic conditions. The deterioration of the crystal occurred only at the surface, because it could be reused after polishing the surface with a diamond paste. The use of a more acid-tolerant ATR crystal (e.g., Ge, diamond) is necessary to surely circumvent the corrosion problem; we, at least, observed similar band changes as observed here when a Ge crystal was used for the acetalization systems (Fig. 10). Nevertheless, the use of Ge is restricted as this material has a very high refractive index (4.0), which decreases the signal drastically compared to ZnSe or diamond and furthermore possesses a low rupture modulus, which limits the use to moderate pressure.³⁰

CONCLUSION

In situ attenuated total reflection infrared spectroscopy has been shown to be a useful tool for tracing the acetalization of cyclohexanone in CO₂-expanded ethylene glycol and methanol at 50 °C and 3 MPa. The spectra of the acetalization mixtures recorded with a ZnSe crystal showed the clear increase and decrease of the bands due to the products and reactants, respectively. In addition, they revealed that the rate of CO₂ dissolution strongly depends on the properties of the alcohols. The method, however, did not afford any mechanistic information, probably due to the extremely low concentrations or short lifetimes of the possible intermediates. Finally, ZnSe was relatively unstable under the acidic conditions realized by the dissolution of CO₂ in the alcohols, and acid-tolerant ATR crystals such as Ge crystal and diamond crystal are much more appropriate for tracing the acetalizations. It was revealed that the spectrum changes with Ge crystal were similar to those recorded with ZnSe crystal.

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