In Situ Formation of Alkylcarbonic Acids with CO_2

Kevin N. West, Christy Wheeler, Jonathan P. McCarney, Kris N. Griffith, David Bush, Charles L. Liotta, and Charles A. Eckert*

Schools of Chemical Engineering and Chemistry and Biochemistry, and Specialty Separations Center, Georgia Institute of Technology, Atlanta, Georgia 30332-0100

Received: October 19, 2000

The mutual solubility of carbon dioxide and alcohols over a wide range of temperature and pressure provides a useful and tunable medium for reactions and separations. For many years, researchers have used alcohols as cosolvents in supercritical CO_2, and recently CO_2-swollen alcohols have been used for antisolvent crystallization and as mobile phases for chromatography. However, little consideration has been given to chemical interaction between the alcohols and CO_2. We have confirmed that such an interaction does exist and can create an acidic environment. By isolating reaction products we have demonstrated that alcohol−CO_2 complexes react similarly to carboxylic acids with diazodiphenylmethane, a compound typically used to evaluate acid strengths. Our evidence indicates that the behavior of CO_2−alcohol systems is comparable to that of CO_2−water systems, where carbonic acid is formed.

Introduction

The addition of short-chain alcohols to supercritical CO_2 to enhance solubility for extractions[1−3] and reactions[4,5] is commonly practiced. Further, CO_2 is used with liquid alcohols to form gas-expanded liquids for particle formation[6] and separations.[7] Although water and CO_2 are known to form carbonic acid, analogous behavior between CO_2 and alcohols has not been well examined. We report here results that constitute strong evidence for the in situ formation of alkylcarbonic acids from CO_2 and alcohols in a supercritical fluid and in swollen liquids.

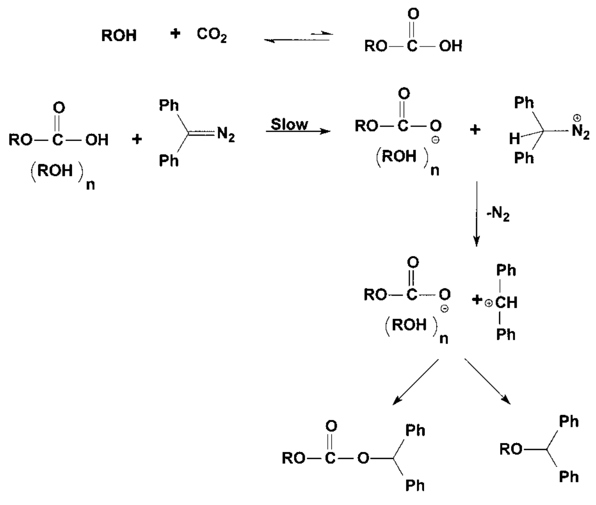
The possible presence of such compounds has not been recognized in explaining cosolvent effects in supercritical fluids nor in acidity in gas-expanded liquids. Methylcarbonic acid is a known compound;[8] it has been shown to exist at low temperatures and to decompose upon melting at −36 °C. Enhanced acidity and solubilization effects in a CO_2−alcohol system may be either beneficial or detrimental to the desired application, which might be reactions, analytical separations, or antisolvent crystallization.

We first postulated the existence of a complex between CO_2 and methanol while examining solvatochromic properties of CO_2−swollen alcohols. The disappearance of color in a methanol solution of Reichardt's Dye upon exposure to CO_2 indicated that a species was present that could protonate the phenoxide ion on the dye. This phenomenon was observed in other short-chain alcohol solvents, but not in polar aprotic solvents.

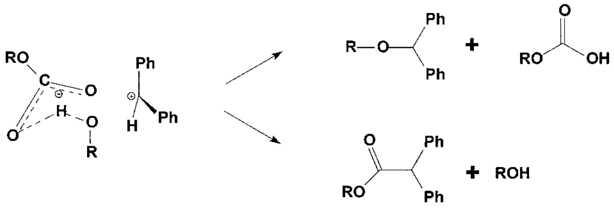
Experimental and Results

To observe the formation of alkylcarbonic acids in CO_2−swollen alcohols, we used diazodiphenylmethane (DDM) as a reactive probe to trap the acid species (Scheme 1). DDM has been used to study steric and substituent effects on acidities of substituted benzoic and naphthoic acids.[9] The rates of reaction of the acids with DDM correlate with relative acid strengths, the rate-limiting step being the protonation of the methyne carbon on DDM. When the reaction is carried out in an alcohol solvent, the ion pair shown in Scheme 2 is formed and then collapses into one of two products: an ether or an ester.

SCHEME 1: Alkylcarbonic Acid Formation and Reaction with Diazodiphenylmethane To Produce the Ether and Carbonate Species



SCHEME 2: Collapse of the Ion Pair To Afford the Ether and Carbonate



With an alkylcarbonic acid, however, the two expected products from the collapse of the intermediate are an ether and a carbonate. Alcohols in the absence of an acid do not react

---

* Corresponding author. E-mail: cae@che.gatech.edu. fax: (404)894-9085.

10.1021/jp003846y CCC: $20.00

TABLE 1: Pseudo-First-Order Rate Constants for the Disappearance of Diazodiphenylmethane in a Mixture of 60% Acetone, 20% CO_2, and 20% R−OH at 40 °C

R	rate 1/s × 10^5
H	1.19
CH_3	3.55
CH_2CH_3	1.89
i-Pr	0.92
t-Bu	0.42

significantly with DDM.[9] Thus, identifying the products of the reaction of DDM in CO_2−swollen methanol can verify the presence of an alkylcarbonic acid.

To show that DDM would react in a CO_2−swollen alcohol solution we first conducted a product analysis. DDM was dissolved into methanol and this solution was pressurized with 70 bar of CO_2 for 2 days at room temperature. The contents were then sampled and analyzed via mass spectrometry and proton NMR, which confirmed that the methyl ether and carbonate were formed in near equal proportions, thus trapping the acid complex. The ethyl ether and ethyl carbonate were formed when this was carried out in ethanol. A similar experiment was performed in supercritical CO_2 at 40 °C and 100 bar with a soluble amount of methanol and the same products were identified.

We measured the relative reaction rates of the alcohols to determine the relative acid strengths of these alkylcarbonic acids. DDM has a strong absorption in the visible region at around 525 nm; the disappearance of this band gives the rate of reaction. To compare the rates to the rate with carbonic acid, acetone was used as a diluent to maintain a single liquid phase. The kinetic measurements were conducted at 40 °C using a solution containing 60 mol % acetone, 20 mol % CO_2, and 20 mol % R−OH. Because the amount of acid remains constant, the reaction was found to be pseudo-first-order with respect to DDM. The pseudo-first-order rate constants are shown in Table 1.

The rates are influenced by both the actual acidity of the acids and the prior equilibria to form the alkylcarbonic acids. We are currently seeking to determine these values so that their effects can be separated. The rates for the reactions run in alcohols follow a logical progression with the fastest rate in methanol and the slowest in *tert*-butyl alcohol. This relationship is consistent with steric and electronic factors affecting the equilibrium and dissociation.

Conclusions

We present new evidence consistent with the in situ formation of alkylcarbonic acids from CO_2 and alcohols in a supercritical fluid and in swollen liquids. Much of the effect of alcohols as cosolvents for supercritical fluid CO_2 and of CO_2 as an antisolvent for liquid alcohols in GAS and separation processes is due to hydrogen bonding interactions. Certainly the concentration in each case of the alkylcarbonic acid is less than that of the alcohol, but these alkylcarbonic acids should be substantially stronger proton donors and acceptors than the alcohols from which they come. We are currently working to determine the concentrations of the alkylcarbonic acids and their equilibrium constants for hydrogen bonding relative to the alcohols to elucidate these effects.

References and Notes

(1) Brennecke, J. F.; Eckert, C. A. *AIChE J.* **1989**, *35*, 1409−1427.
(2) Ekart, M. P.; Bennett, K. L.; Ekart, S. M.; Gurdial, G. S.; Liotta, C. L.; Eckert, C. A. *AIChE J.* **1993**, *39*, 235−248.
(3) Eckert, C. A.; Knutson, B. L.; Debenedetti, P. G. *Nature* **1996**, *383*, 313−318.
(4) Dillow, K.; Hafner, K. P.; Yun, S. L. J.; Deng, F.; Kazarian, S. G.; Liotta, C. L.; Eckert, C. A. *AIChE J*, **1997**, *43*, 515−524.
(5) Eckert, C. A.; Chandler, K. *J. Supercrit. Fluids* **1998**, *13*, 187−195.
(6) Reverchon, E.; Della, G. *Powder Technol.* **1999**, *106*, 23−29.
(7) Chang, C. J.; Randolph, A. D. *Biotechnol. Prog.* **1991**, *7*, 275−278.
(8) Gattow, G.; Behrendt, W. *Angew. Chem.* **1972**, *84*, 549−550.
(9) Chapman, N. B.; Rodgers, M. G.; Shorter, J. *J. Chem. Soc. B* **1968**, 164−167.