

Excited-State Proton Transfer in Gas-Expanded Liquids: The Roles of Pressure and Composition in Supercritical CO₂/Methanol Mixtures

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Molecules that increase their acidity constant upon electronic excitation ($pK_a^* < pK_a$) have been known for half a century¹ and have contributed significantly to our understanding of proton transfer in aqueous solutions.² Recent advances in this area have focused on excited-state proton transfer (ESPT) in organic media, making use of a new generation of photoacids ($pK_a^* < 0$)³ such as the remarkable “super” photoacid, 5,8-dicyano-2-naphthol (DCN2). Unlike the parent 2-naphthol, DCN2 combines a remarkably strong acidity ($pK_a^* = -4.5$ in aqueous solution) with very fast proton transfer to organic solvents and very intense fluorescence for both nondissociated (R^*OH) and anionic (R^*O^-) forms.⁴ Such super photoacids raise the possibility of inducing proton jumps in cosolvent-modified supercritical fluids or in gas-expanded liquids. In view of the growing importance of supercritical carbon dioxide ($scCO_2$) as a processing solvent and as a reaction medium, particularly for reactions involving proton transfer, and of the interest in adding cosolvents to tailor the properties of $scCO_2$, we now report the proton-transfer properties of DCN2 in MeOH/ CO_2 mixtures, using methanol mole fractions (X_{MeOH}) ranging from 0.2 to 0.7. ESPT in MeOH/ CO_2 mixtures has been attempted using 2-naphthol and 5-cyano-2-naphthol (5CN2), but the authors failed to detect any naphtholate emission.⁵ The success of the present work is tied to the much higher acidity of DCN2.

Absorption, fluorescence, and single-photon counting measurements of DCN2 in MeOH/ CO_2 mixtures at temperatures between 307 and 330 K and pressures between 9.5 and 25 MPa followed standard procedures.^{6,7} Mole fractions X_{MeOH} at 323 K were calculated from the MeOH volume in the cell at room temperature and the density of MeOH/ CO_2 mixtures at this temperature.⁸ Visual inspection ensured that a single phase was present in all the experiments. The pressures and temperatures in this study were in the supercritical region of CO_2 .

DCN2 in $scCO_2$ has only one fluorescence band, with a maximum at 395 nm, assigned to R^*OH . With the addition of MeOH the R^*OH emission maximum first shifts to 440 nm, and at a minimum concentration of MeOH, a new emission, assigned to R^*O^- , was observed at 580 nm, Figure 1. The positions of these maxima were virtually the same for all the MeOH/ CO_2 mixtures measured in this work. In pure methanol, these two bands were observed at 440 and 600 nm, respectively. The frequencies of the R^*OH emission maxima of naphthols were correlated with the polarizability (π^*) and the hydrogen-bond accepting/electron-pair donating (β) parameters of Taft.⁹ The 2590 cm^{-1} shift observed from methanol to $scCO_2$ was larger than the 2350 cm^{-1} shift reported for 5CN2 when the solvent was changed from methanol to hexane. The very low polarizability of $scCO_2$ (π^* values between -0.1 and -0.4 in the 9.5–25 MPa pressure range)^{10a} favors such

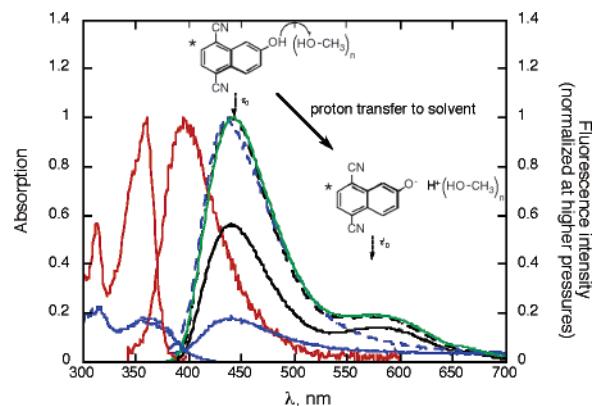


Figure 1. Fluorescence excitation and emission of DCN2 in $scCO_2$ at 8.4 MPa and 312 K (red). Absorption and fluorescence of DCN2 in MeOH/ CO_2 for $[MeOH]/M = 3$ (blue), 14 (black), and pure methanol (green). MeOH/ CO_2 mixtures at 307 K and 12 MPa (full lines) or 25 MPa (dashed lines); MeOH: 298 K under a 12 MPa pressure of CO_2 .

large shifts, when combined with a low β . The value of β of $scCO_2$ remains controversial. Hyatt compared it to that of an ether,^{10b} but Maiwald and Schneider reported $\beta = 0$.^{10c} Only $\beta \approx 0$ can reconcile the shift of DCN2 in $scCO_2$ with the values for 5CN2. The modest hypsochromic shift of the R^*O^- emission suggests that DCN2 is only ca. 1 pK_a unit less acidic in MeOH/ CO_2 mixtures than in pure methanol. Protolytic photodissociation of highly acidic DCN2 in methanol-poor mixtures suggests the existence of MeOH aggregates and preferential solvation of DCN2 by such aggregates. Evidence for MeOH aggregates was also found in organic liquid and sc solvents.¹¹ The full extent of the H-bonded aggregates is already observed at very low methanol concentrations.

The ratio of R^*O^- and R^*OH fluorescence intensities, I_A/I_N in Figure 2, which is directly proportional to the ESPT rate constant,^{1b} decreases with decreasing X_{MeOH} . The lower X_{MeOH} values seem to extrapolate linearly to 0 and reveal that very small methanol mole fractions are needed for proton transfer to methanol. This supports the preferential solvation of DCN2 by a cluster of methanol molecules. The extrapolation to pure methanol at high pressures leads to a lower ratio than that reported by Huppert et al. for DCN2 in propanol at higher pressures.^{12a} We assign this to the presence of oxygen in our system. The scatter in Figure 2 reflects the reproducibility of independent measurements. This scatter is much lower within single experimental runs. The results discussed below focus on comparisons within experimental runs.

The I_A/I_N ratios remain virtually unchanged when the temperature changes from 307 to 330 K. Thus, temperature effects play only a minor role in our systems.⁷ This is expected in view of the insensitivity of the deprotonation rate of DCN2 in methanol to temperatures above the diffusion limit.^{12b} However, Figure 3 shows

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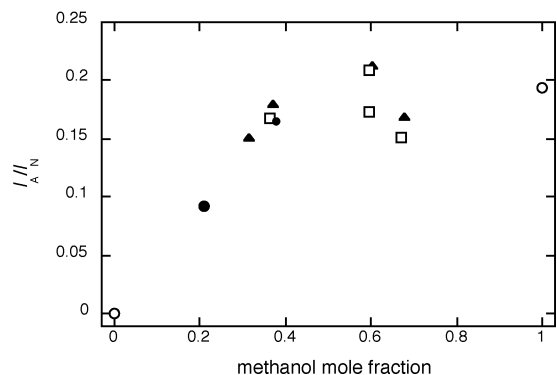


Figure 2. Ratio of R*O⁻ and R*OH fluorescence intensities as a function of MeOH mole fraction. Measured at $T = 323$ K and $P/\text{MPa} = 12$ (circles), 17.5 (triangles), and 22 (squares).

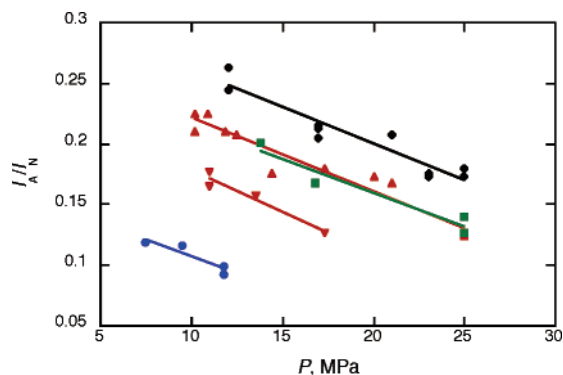


Figure 3. Ratio of R*O⁻ and R*OH fluorescence intensities as a function of pressure. Measured between 307 and 330 K and $[\text{MeOH}]/M = 4$ (circles), 8 (triangles), 12 (squares), and 14 (lozenges).

that an increase in pressure leads to a very pronounced decrease in the I_A/I_N ratio. The increase in pressure is also a dilution of methanol. For example, in the experimental run with the largest amount of MeOH, the increase in pressure from 12 to 25 MPa at 307 K corresponds to a decrease in mole fraction from 0.64 to 0.60. Figure 2 indicates that such a decrease should lead to not more than a 10% decrease in the I_A/I_N ratio, but a 26% decrease is observed. Furthermore, the fluorescence intensity of R*OH almost doubles with this increase in pressure, whereas that of R*O⁻ increases very little. Thus, the I_A/I_N ratio decreases with an increase in pressure mostly because I_N increases with pressure.

We measured the lifetimes of R*OH and R*O⁻ both at 11 and 25 MPa, for $T = 307$ K and $[\text{MeOH}] = 14$ M. The decays observed at 440 nm for R*OH were nonexponential,⁷ with the characteristic tail observed in methanol and assigned to reversible proton geminate recombination.¹³ The full kinetic analysis of these decays requires information on diffusion coefficients and dielectric constants of MeOH/CO₂ mixtures, not readily available. However, from a multiexponential fit of the decays, we estimate average lifetimes of 1.3 ns at 11.5 MPa and 2.8 ns at 25 MPa (χ -squares of 1.03 and 1.10, respectively). In MeOD/CO₂ mixtures these average lifetimes increase to 2.3 and 3.1 ns, respectively. The increase of these lifetimes with pressure is consistent with the concomitant decrease in the I_A/I_N ratio. They approach the lifetimes measured in racemic 2-butanol, where a similar I_A/I_N ratio was also observed. The kinetic isotope effects (KIE) are low, $\text{KIE} < 2$, as expected from the nearly temperature-independent I_A/I_N ratio. The R*O⁻ emission at 570 nm reveals rise times and monoexponential decays; the latter have lifetimes of 2.0 ns at 11 MPa and 3.0 ns at 25 MPa (χ -squares of 1.20 and 1.37). In MeOD/CO₂ mixtures these lifetimes increase to 3.3 and 3.6 ns, respectively, again indicating low KIE. Thus, proton-

transfer dynamics in MeOH/CO₂ are characterized by low kinetic barriers, but these tend to increase with pressure.

The effect of pressure on the deprotonation rate of DCN2 in ethanol and propanol has been studied by Huppert and co-workers.^{12a,c} They find that, at low pressures, the R*OH lifetime decreases with pressure but that at higher pressures the opposite is observed. Their “low pressures” extend to 700 MPa and include the whole range of our pressures. These authors also observe an increase in R*OH fluorescence intensity with pressure. We assign the decrease in the I_A/I_N ratio with pressure to an increase in the R*OH fluorescence intensity, due to less efficient proton transfer at higher pressures. Huppert and co-workers suggest the opposite, arguing for efficient proton tunneling at higher pressures. Our differences can be explained by the high compressibility of MeOH/CO₂ mixtures, where pressure will disrupt the methanol clusters rather than bring methanol and DCN2 molecules closer together to promote tunneling. Johnston and Fox found little, if any, deprotonation of 2-naphthol in scH₂O and assigned this to the loss of local water structure at elevated temperatures and pressures.¹⁴ The loss of local structure may justify the effect of pressure in the I_A/I_N ratio and in the R*OH lifetime observed in this study. A more complete kinetic analysis is in progress, aiming at a full characterization of the reaction dynamics in this fluid.

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Supporting Information Available: Experimental procedures, temperature and additional pressure dependences of I_A/I_N , and single-photon counting decays of R*OH and R*O⁻. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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