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Photo-Fries Rearrangement of Naphthyl Acetate in Supercritical Carbon Dioxide: Chemical Evidence for Solvent−Solute Clustering[1]

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The critical temperature (T_C) of a substance defines the last point on the liquid−vapor curve of its phase diagram; below this temperature the gas and liquid phases can exist in equilibrium, and compression of the gas ultimately results in liquefaction. Above T_C, the fluid is said to be in its supercritical phase, and compression results in increased density but does not lead to phase separation.[2] Sufficiently dense supercritical fluids have the ability to dissolve relatively nonvolatile solutes, and this has led to their development as alternatives to organic solvents for extraction in chemical[3a] and biotechnological[3b,c] processes and as mobile phases for chromatography.[4] For the chemist, supercritical fluids offer exciting possibilities because variations in the density, viscosity, diffusivity, and dielectric properties can be induced simply by varying the pressure or the temperature; these variations are particularly dramatic in the region just above the critical point and potentially can alter the rate or course of chemical processes.[5]

One of the properties of supercritical fluids that has attracted considerable recent attention is the local solvent density augmentation around solute molecules which seems to occur in the near-critical region. The possibility of such a clustering phenomenom was initially proposed to explain very large negative partial molar volumes observed for solutes dissolved in supercritical fluids at temperatures and pressures close to the critical point.[6] Subsequently, studies using steady state absorption spectroscopy and steady state and time-resolved emission spectroscopy have revealed strong evidence for *increased* local solvent densities around solute molecules as the pressure (and hence the density) of a supercritical fluid is *lowered* in the region just above the critical point.[7−9]

The clustering phenomenon would be expected to give rise to cage effects in chemical reactions conducted in supercritical fluids, and attempts have been made to detect these effects. Two studies of the photochemical dimerization reaction of 2-cyclohexenones in supercritical media have found that the quantum yield of dimer formation and also the product distribution exhibit a pressure dependency.[10,11] This has been interpreted as evidence for enhanced solvent−solute interactions between the enone excited state and its ground state partner at lower fluid densities. However, other interpretations are also possible since the enone dimerization reaction involves the intermediacy of triplet 1,4-biradicals that partition between products and starting materials. The factors that govern the properties of these intermediate 1,4-biradicals are not fully understood; however, they are certainly medium dependent and control both the product distribution and the reaction efficiency.[12]

As far as we are aware, the only other reaction system which has been used to probe the existence of solute−solvent clusters in supercritical fluids is the Norrish type I photochemical cleavage of unsymmetrical dibenzyl ketones.[13] In this system, photolysis produces a benzyl radical and a phenacyl radical; decarbonylation of the latter generates a second benzyl radical. Coupling of the benzyl radicals to give dibenzyls can occur within a solvent cage or following cage escape. In supercritical fluids, no evidence of in-cage recombination is observed, even when the density of the fluid is lowered to the region where clusters are thought to exist. Brennecke and Chateauneuf have pointed out that this does not necessarily mean that clusters do not form, since their lifetime may be much shorter than the time required for the decarbonylation reaction of the phenacyl radical.[13a] It has been calculated that the lifetime of supercritical fluid clusters is of the order of a few picoseconds,[14] while the time required for decarbonylation of the phenacyl radical has been measured by laser flash photolysis[13a] and is $\sim$100 ns. Consequently, an acyl−phenacyl radical pair would have separated long before the decarbonylation event so that in-cage combination of benzyl radicals becomes impossible.

We have attempted to avoid this problem by using the photo-Fries rearrangement reaction of 1-naphthyl acetate.[15a−e] As shown in Scheme 1, this reaction occurs from the singlet excited state *via* a much shorter-lived singlet radical pair estimated to have a lifetime of 25 ps.[15c] In the absence of a solvent cage to

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(2) Reid, R. C.; Prausnitz, J. M.; Poling, B. E. *The Properties of Gases and Liquids*, 4th ed.; McGraw-Hill: New York, 1987.

(3) (a) McHugh, M. A.; Krukonis, V. J. *Supercritical Fluid Extraction: Principles and Practices*; Butterworths: Stoneham, 1986. (b) Choi, K. J.; Nakhost, Z.; Krukonic, V. J.; Karel, M. *Food Biotechnol.* **1987**, *1*, 263. (c) Larson, K. A.; King, M. L. *Biotechnol. Prog.* **1986**, 73.

(4) *Supercritical Fluid Chromatography*; Smith, R. M., Ed.; Royal Society of Chemistry Monograph; Royal Society of Chemistry: London, 1988.

(5) (a) Brennecke, J. F. In *Supercritical Fluid Engineering Science: Fundamentals and Applications*; Kiran, E., Brennecke, J. F., Eds.; ACS Symposium Series 514; American Chemical Society: Washington, DC, 1993; Chapter 1. (b) Bright, F. V.; McNally, M. E. P. In *Supercritical Fluid Technology: Theoretical and Applied Approaches to Analytical Chemistry*; Bright, F. V., McNally, M. E. P., Eds.; ACS Symposium Series 488; American Chemical Society: Washington, DC, 1992; Chapter 1. (c) Bruno, T. J.; Ely, J. F. *Supercritical Fluid Technology: Reviews in Modern Theory and Applications*; CRC Press: Boca Raton, FL, 1991.

(6) (a) Ehrlich, P.; Fariss, R. *J. Phys. Chem.* **1969**, *73*, 1164. (b) Wu, P. C.; Ehrlich, P. *AIChE J.* **1973**, *19*, 533. (c) Eckert, C. A.; Ziger, D. H.; Johnston, K. P.; Ellison, T. K. *Fluid Phase Equilib.* **1983**, *14*, 167. (d) Eckert, C. A.; Ziger, D. H.; Johnston, K. P.; Kim, S. *J. Phys. Chem.* **1986**, *90*, 2738.

(7) (a) Yonker; C. R.; Frye, S. L.; Kalkwarf, D. R.; Smith, R. D. *J. Phys. Chem.* **1986**, *90*, 3022. (b) Yonker, C. R.; Smith, R. D. *J. Phys. Chem.* **1988**, *92*, 2374. (c) Kim, S.; Johnston, K. P. *AIChE J.* **1987**, *33*, 1603.

(8) (a) Hrnjez, B. J.; Yazdi, P. T.; Fox, M. A.; Johnston, K. P. *J. Am. Chem. Soc.* **1989**, *111*, 1915. (b) Sun, Y.-P.; Fox, M. A.; Johnston, K. P. *J. Am. Chem. Soc.* **1992**, *114*, 1187. (c) Sun, Y.-P.; Bennett, G.; Johnston, K. P.; Fox, M. A. *J. Am. Chem. Soc.* **1992**, *96*, 10001.

(9) (a) Zagrobelny, J.; Betts, T. A.; Bright, F. V. *J. Am. Chem. Soc.* **1992**, *114*, 5249. (b) Zagrobelny, J.; Bright, F. V. *J. Am. Chem. Soc.* **1992**, *114*, 7821. (c) Betts, T. A.; Zagrobelny, J.; Bright, F. V. *J. Am. Chem. Soc.* **1992**, *114*, 8163. (d) Zagrobelny, J.; Bright, F. V. *J. Am. Chem. Soc.* **1993**, *115*, 701.

(10) Combes, J. R.; Johnston, K. P.; O'Shea, K. E.; Fox, M. A. In ref 5b, Chapter 3.

(11) Hrnjez, B. J.; Mehta, A. J.; Fox, M. A.; Johnston, K. P. *J. Am. Chem. Soc.* **1989**, *111*, 2662.

(12) (a) Hastings, D. J.; Weedon, A. C. *J. Am. Chem. Soc.* **1991**, *113*, 8525. (b) Andrew, D.; Hastings, D. J.; Oldroyd, D. L.; Rudolph, A.; Weedon, A. C.; Wong, D. F.; Zhang, B. *Pure Appl. Chem.* **1992**, *64*, 1327. (c) Maradyn D.; Weedon, A. C. *Tetrahedron Lett.* **1993**, *34*, 2413. (d) Krug, P.; Rudolph, A.; Weedon, A. C. *Tetrahedron Lett.* **1993**, *34*, 7221.(e) Rudolph, A.; Weedon, A. C. *Can. J. Chem.* **1990**, *68*, 1590.(f) Andrew, D.; Hastings, D. J.; Weedon, A. C. *J. Am. Chem. Soc.* **1994**, *116*, 10870.

(13) (a) O'Shea, K. E.; Combes, J. R.; Fox, M. A.; Johnston, K. P. *Photochem. Photobiol.* **1991**, *54*, 571. (b) Roberts, C. B.; Zhang, J.; Brennecke, J. F.; Chateauneuf, J. E. *J. Phys. Chem.* **1993**, *97*, 5618. (c) Roberts, C. B.; Zhang, J.; Chateauneuf, J. E.; Brennecke, *J. Am. Chem. Soc.* **1993**, *115*, 9576.

(14) Petsche, I. B.; Debenedetti, P. G. *J. Chem. Phys.* **1989**, *91*, 7075.

(15) (a) Ohto, Y.; Shizuka, H.; Sekiguchi, S.; Matsui, K., *Bull. Chem. Soc. Jpn.* **1874**, *47*, 1209. (b) Crouse, D. J.; Hurlbut, S. L.; Wheeler, D. M. S. *J. Org. Chem.* **1981**, *46*, 374. (c) Nakagaki, R.; Hiramatsu, M.; Watanabe, T.; Tanimoto, Y.; Nagakura, S. *J. Phys. Chem.* **1985**, *89*, 3222. (d) Sakaguchi, Y.; Hayashi, H.; Nakagura, S. *Bull. Chem. Soc. Jpn.* **1980**, *53*, 39. (e) Bellus, D. *Adv. Photochem.* **1971**, *8*, 109. (f) Coppinger, G. M.; Bell, E. R. *J. Phys. Chem.* **1966**, *70*, 3479. (g) Meyer, J. W.; Hammond, G. S. *J. Am. Chem. Soc.* **1970**, *92*, 2189. (h) Humphrey, J. S.; Roller, R. S. *Mol. Photochem.* **1971**, *3*, 35.

0002-7863/95/1517-6132$09.00/0

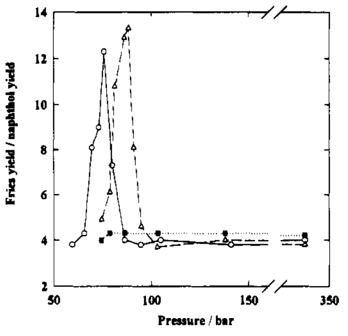

Figure 1. Pressure dependence of the ratio of the photo-Fries product yield to 1-naphthol yield for the photolysis of 1-naphthyl acetate (1.80 × 10^{-3} M) in carbon dioxide containing 2-propanol (0.073 M). ■, T = 27 °C; ○, T = 35 °C; △, T = 47 °C. Product yields were determined directly by gas chromatography and are uncalibrated. Uncertainty in product ratios is ~5–10%.

Scheme 1

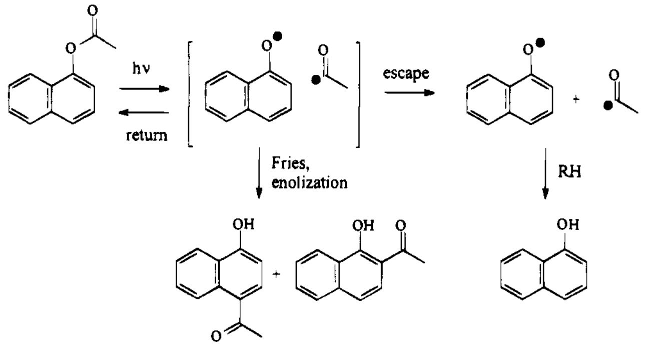

Table 1. Product Ratios Obtained in the Photolysis of 0.003 M Naphthyl Acetate in Supercritical CO_2 at 35 °C[a]

	P = 76 bar		P = 103 bar	
cosolvent	Fries/ naphthol	ortho/ para	Fries/ naphthol	ortho/ para
none	2.8 ± 0.4	0.8 ± 0.1	1.4 ± 0.1	0.91 ± 0.06
0.0044 M Me_2CHOH	3.7 ± 0.3	1.2 ± 0.1	2.18 ± 0.07	1.13 ± 0.02
0.018 M Me_2CHOH	4.9 ± 0.3	1.51 ± 0.08	2.28 ± 0.07	1.84 ± 0.05
0.088 M Me_2CHOH	5.9 ± 0.3	1.79 ± 0.07	2.9 ± 0.1	2.68 ± 0.06
0.013 M C_6H_6	2.6 ± 0.2	0.74 ± 0.03	1.5 ± 0.2	0.98 ± 0.09
0.011 M $PhCH_2OH$	3.1 ± 0.3	0.97 ± 0.09	1.4 ± 0.1	0.93 ± 0.07
0.139 M MeOH	8.5 ± 0.8	1.34 ± 0.07	2.5 ± 0.2	3.2 ± 0.2
0.012 M Bu^tOH	2.9 ± 0.2	0.85 ± 0.03	2.02 ± 0.08	1.32 ± 0.05

[a] Products were analyzed by gas chromatography relative to a calibrated internal standard added following silylation of naphthol, 2-acetylnaphthol ("ortho"), and 4-acetylnaphthol ("para"). The same experiment performed in liquid CO_2 (27 °C and 76 bar) containing 0.088 M 2-propanol gave a Fries/naphthol ratio of 2.7 ± 0.3 and an ortho/para ratio of 2.7 ± 0.2

maintain the proximity of the radicals, they can diffuse apart and generate naphthol by abstraction of a hydrogen atom from a suitable donor. However, in a medium that restricts mobility, recombination or rearrangement also occurs so that the proportions of escape products and Fries rearrangement products can be used to probe the efficiency of cage escape.[15f–h]

Photolysis[16] of 1-naphthyl acetate (1.80 × 10^{-3} M) in *liquid* carbon dioxide (T = 27 °C) containing 2-propanol[17] (0.073 M) at 75–345 bar resulted in the formation of naphthol, 2-acetylnaphthol, and 4-acetylnaphthol as the only products.[18] The ratio of the cage escape product (i.e., naphthol) to the in-cage rearrangement products (i.e., 2- and 4-acetylnaphthol) was constant over the entire pressure range examined. These experiments were repeated at 35 and 47 °C, which are above the critical temperature of pure carbon dioxide (T_C = 31.19 °C); in these supercritical phases, the yield of 1-naphthol relative to the combined yield of the photo-Fries rearrangement products was found to decrease dramatically as the pressure approached the critical pressure of pure carbon dioxide, 73.8 bar. The results of these experiments are shown in Figure 1.

Similar results were also obtained when 2-propanol was not present (Figure 2, supplementary material).[19] The ortho to para ratio (i.e., 2-acetylnaphthol:4-acetylnaphthol) showed no great variation with pressure in the absence of 2-propanol. However, in the presence of 2-propanol, the ratio was perturbed (Table 1). Variation of the 2-propanol concentration had little effect on the Fries:naphthol ratio at >110 bar;[17] at lower pressures, the increase in the proportion of photo-Fries rearrangement (i.e., in-cage) product formed was enhanced relative to the cage escape product (i.e., naphthol) by increasing 2-propanol concentration (Table 1). Addition of methanol had a similar effect, while addition of small amounts of other cosolvents (benzene, benzyl alcohol, *tert*-butanol) had no effect on the photo-Fries product:naphthol ratio (Table 1).

The data illustrated in Figures 1 and 2 are counterintuitive, since it would be expected that the proportion of the cage escape product 1-naphthol should increase as the pressure (and hence the bulk density) of the supercritical solution is lowered; in fact, the apparent solvent cage effect on the product ratios increases at the lower supercritical fluid bulk densities. This is consistent with the existence of supercritical solvent–solute clusters with a lifetime comparable with or longer than that of the singlet radical pair produced in the reaction.

The variation in product ratio observed for the 1-naphthyl acetate reaction correlates well with data reported by Eckert and co-workers for the variation with pressure of the partial molar volume of naphthalene in supercritical carbon dioxide.[6] Figure 3 (supplementary material) shows a comparison of our data with those of Eckert. The large change in the partial molar volume which occurs in the region just above the critical pressure was ascribed to the formation of solvent–solute clusters and coincides with the increased relative yield of the in-cage products produced in the photolysis of 1-naphthyl acetate.

The effect of 2-propanol and methanol on the product ratios may be interpreted in terms of solute–solute interactions involving hydrogen bonding within solute–solvent clusters; the absence of these effects when other, less polar additives are present may reflect dominance of solute–solvent interactions over solute–solute interactions for these systems.

The results reported here suggest that the formation of solute–solvent clusters in supercritical fluids can indeed perturb the outcome of a chemical reaction, but only if the competing, product-selecting steps are rapid and occur in a time comparable to or shorter than the effective lifetime of the clusters.

Supplementary Material Available: Figures 2 and 3, as described in the text (3 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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[16] Photolyses were performed employing quartz and water-filtered light from a 100 W high-pressure mercury lamp which was focused onto the quartz window of a thermostated high-pressure cell containing the naphthyl acetate solution.

[17] The 2-propanol was added as a hydrogen atom donor. In supercritical carbon dioxide at 40 °C and 110 bar, the product ratio was unaffected when the 2-propanol concentration was varied from 0.02 to 0.3 M. A single phase was observed throughout this range.

[18] Products were identified by GC and GC/MS comparison with authentic samples. Conversions of 1-naphthyl acetate were in the range 7–12%. Mass balances were greater than 99%.

[19] In the absence of 2-propanol as a hydrogen atom donor, the acyl and naphthyloxy free radicals resulting from cage escape are presumed to be quenched by disproportionation, abstraction from impurities, at the vessel walls, etc. No other products were detected in the reaction mixture, and no evidence for termination of the naphthyloxy radical by dimerization, addition to naphthyl acetate, etc. was found.