

ORGANIC CHEMISTRY IN SUPERCRITICAL FLUID SOLVENTS:  
PHOTOISOMERIZATION OF trans-STILBENE

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INTRODUCTION

The unusual solvent properties of supercritical fluids (SCF's) have been known for over a century (1). Just above the critical temperature, forces of molecular attraction are balanced by kinetic energy; and fluid properties, including solvent power, exhibit a substantial pressure dependence. Many complex organic materials are soluble at moderate pressures (80 to 100 atmospheres); and SCF solvent power increases dramatically when the pressure is increased to 300 atmospheres. The pressure responsive range of solvent properties thus attainable has provided the basis for investigating the fundamental nature of molecular interactions and, more recently, for exploitation of supercritical fluids in areas of applied research (2,3).

In the latter activity, supercritical fluids have been utilized extensively in the thermochemical solubilization of coal (4), for selective extraction of naturally occurring materials (5,6), and in various separation techniques including distraction (7) and supercritical fluid chromatography (8,9). The physicochemical principles underlying these applications have also been investigated (10). In view of the high level interest in manipulating complex organic mixtures with supercritical fluids, it is surprising that these fluids have seen little use as solvents for organic reactions (11,12). The pivotal role of solvent properties in controlling the course and rate of chemical reactions is well established (13); and, thus, the same kind of pressure responsive solvent-solute interactions which control extractions and separations in SCF's can be expected to direct chemical pathways and influence reaction rates.

Moreover, much of our understanding of the nature of chemical reactions has been derived by observing the responses of these processes to changes in solvent properties. While investigations of this type have been highly productive, interpretation of the results has often been blurred by uncertainties inherent in the experimental approach. Heretofore, liquid solvents have been used in these investigations, and solvent properties have been changed by adjusting the solvent composition. Unfortunately, no quantitative relationship between bulk solvent properties and chemical phenomena has emerged, presumably due to selective solvent-solute interactions which result in differences between bulk solvent composition and microscopic solvent composition (13).

In contrast to liquid solvents, the properties of a single SCF solvent can be altered over a wide range through modest manipulations of pressure and/or temperature. Thus, SCF's provide an opportunity to investigate the effects of solvent properties on chemical reactions without changing the solvent composition. Experimentally, in order to

induce the greatest response of solvent properties to changes in pressure, it is generally best to operate at a constant reduced temperature,  $T_R$ , between 1.0 and 1.1 and to vary the reduced pressure,  $P_R$ , between 1.0 and 3.0 (14).

For several reasons, we chose carbon dioxide for these initial investigations. In the first place, the properties of supercritical carbon dioxide are well known, and the solubility of a relatively large number of organic materials have been examined in this medium. Secondly, although carbon dioxide is interactive with solute molecules, it is generally unreactive. Finally, the supercritical working range ( $1.0 < T_R < 1.1$ ), 31.5 to 60°C, is experimentally convenient; and many organic reactions have been extensively investigated in this temperature range.

Investigations of organic reactions in supercritical solvents are subject to several constraints, one attributable to supercritical fluid properties and others imposed for interpretive and experimental simplicity. Because supercritical fluid properties are affected by changes in temperature, a reaction should be selected which does not require heat for initiation and is not highly exothermic. Secondly, for experimental simplicity and clarity of interpretation, a clean, well understood reaction should be chosen; and one should expect an experimentally observable response to changes in pressure. Finally, a unimolecular reaction which produces a single product obviates the complication of controlling the concentrations of two reactants and simplifies product analysis. The photoisomerization of trans-stilbene meets these requirements.

The photoisomerization of stilbene is one of the most extensively studied and best understood photoreactions (15). Solvent effects have been thoroughly investigated for both the direct and photosensitized isomerizations, and a model has been developed which attributes these effects to solvent viscosity (16). Increased viscosity inhibits direct photoisomerization of the cis isomer, but facilitates that of trans-stilbene. As a result, the cis/trans ratio of the photostationary state increases with increasing solvent viscosity. The wide range of viscosities which are attainable by pressure manipulation of supercritical carbon dioxide provides an excellent opportunity to probe the effect of viscosity on stilbene photochemistry in the same solvent.

## EXPERIMENTAL

Construction of the SCF photochemical reactor and experimental techniques are described elsewhere (12). Photoisomerizations were carried out using a 450 watt Hanovia medium pressure mercury source, and each reaction was followed to the photostationary state by gas chromatographic determination of the cis/trans ratios.

## RESULTS & DISCUSSION

A widely used method for assessing supercritical fluid phenomena consists of comparing physical and chemical behavior above the critical point with corresponding behavior in the subcritical liquid. Because this approach (unrealistically) seeks to observe discontinuous behavior between states, the results of such experiments are often ambiguous. In the present study, we have compared the photoisomerization of trans-stilbene in subcritical and supercritical CO<sub>2</sub>; and, as a

model for condensed phase behavior, we have also carried out these isomerizations in cyclohexane. In all three systems, we have probed and compared the effects of temperature, concentration, and, most significantly, pressure on the photostationary state as reflected in the cis/trans ratio. The results from these experiments are shown in Tables 1 and 2 and are plotted in Figures 1 through 3.

From the results obtained in cyclohexane (Table 1), it is clear that, in the condensed phase, we can expect very little effect on the photostationary state due to changes in temperature or concentration. On the other hand, these factors cause large changes when the reaction is carried out in liquid or (especially) SCF CO<sub>2</sub>. The contrast in behavior is even more apparent in Figures 1 and 2.

**Table 1. Photoisomerization of trans-Stilbene in Cyclohexane<sup>a</sup>**

Initial Concentration (mg/ml) <sup>b</sup>	Temperature (°C)	Irradiation Time (Minutes)	Photostationary State (cis/trans)
2.14	21.7	70.0	6.1
2.14	40.0	70.0	6.1
1.07	21.7	20.0	6.9
1.07	40.0	30.0	6.9
0.50	21.7	10.0	6.4
0.50	40.0	15.0	6.7
0.25	21.7	10.0	6.4
0.25	40.0	5.0	6.6

a. Direct irradiation with a Hanovia 450 watt medium pressure mercury vapor lamp.

b. Pure trans-stilbene was used.

**Table 2. Photoisomerization of trans-Stilbene in Carbon Dioxide<sup>a</sup>**

Initial Concentration (mg/NL) <sup>b</sup>	Reactor Concentration (mg/ml) <sup>c</sup>	Temperature (°C)	Photostationary State (cis/trans)
2.00	0.98	25	8.63
2.00	0.87	40	8.68
0.80	0.39	25	7.15
0.40	0.20	25	6.42
0.40	0.17	40	6.73
0.28	0.13	35	5.66
0.28	0.12	40	6.54
0.28	0.11	50	7.04
0.24	0.10	40	6.29
0.12	0.052	40	4.80

a. Irradiation in a flow reactor with a 450 watt Hanovia medium pressure mercury vapor lamp.

b. Pure trans-stilbene was used. Normal liter (NL): the quantity of CO<sub>2</sub> which has a volume of 1 liter at 25°C and 1 atmosphere.

c. Calculated from the reported density of pure CO<sub>2</sub>.

In Figure 3 is shown the effect of pressure on the cis/trans ratio. While there is a noticeable effect on liquid CO<sub>2</sub>, the dramatic response of the ratio to decreases in pressure gives us a clear signal that we can expect to manipulate chemical pathways, rates, and equilibria in the SCF state. This will be the focus of future studies.

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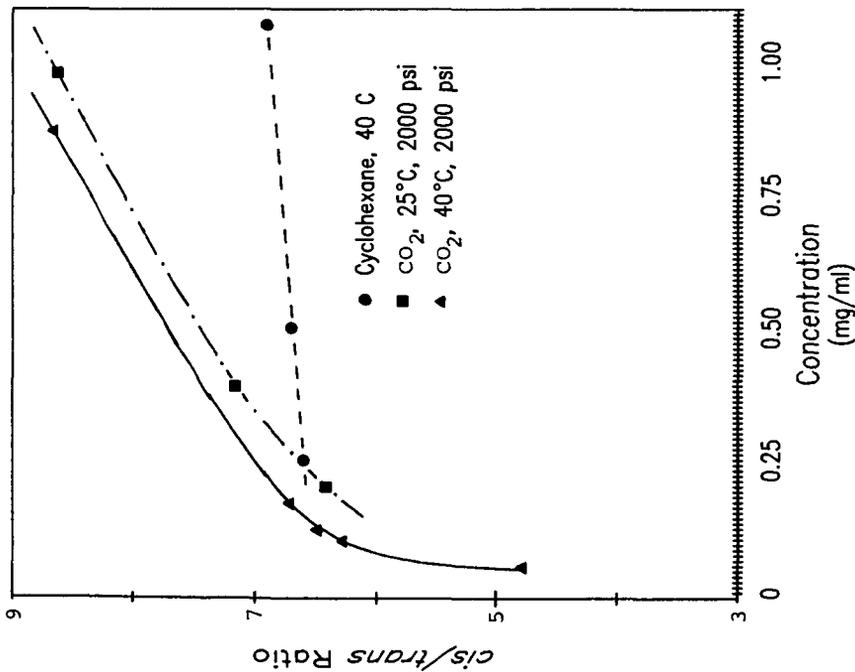


Figure 1. Concentration Effects in the Photoisomerization of trans-Stilbene.

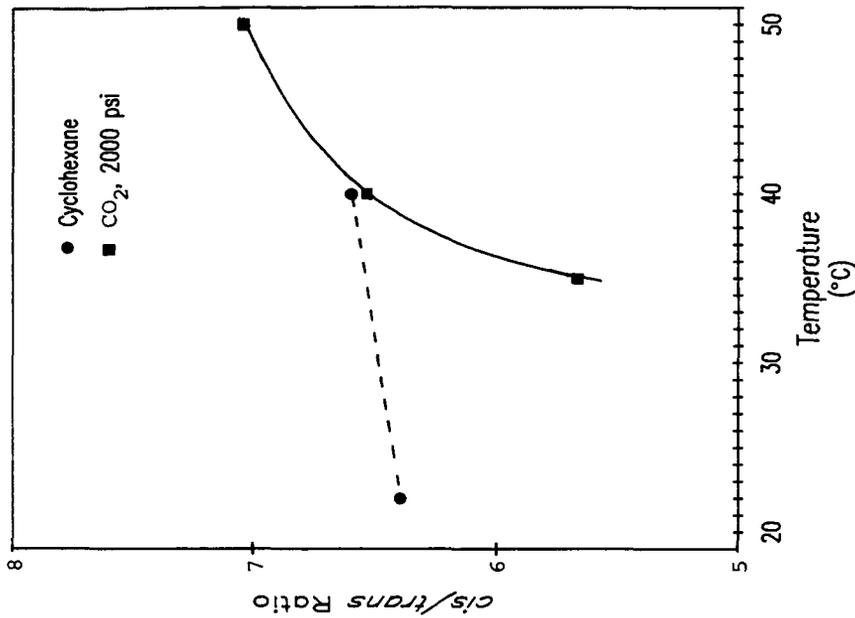


Figure 2. Temperature Effects in the Photoisomerization of trans-Stilbene.

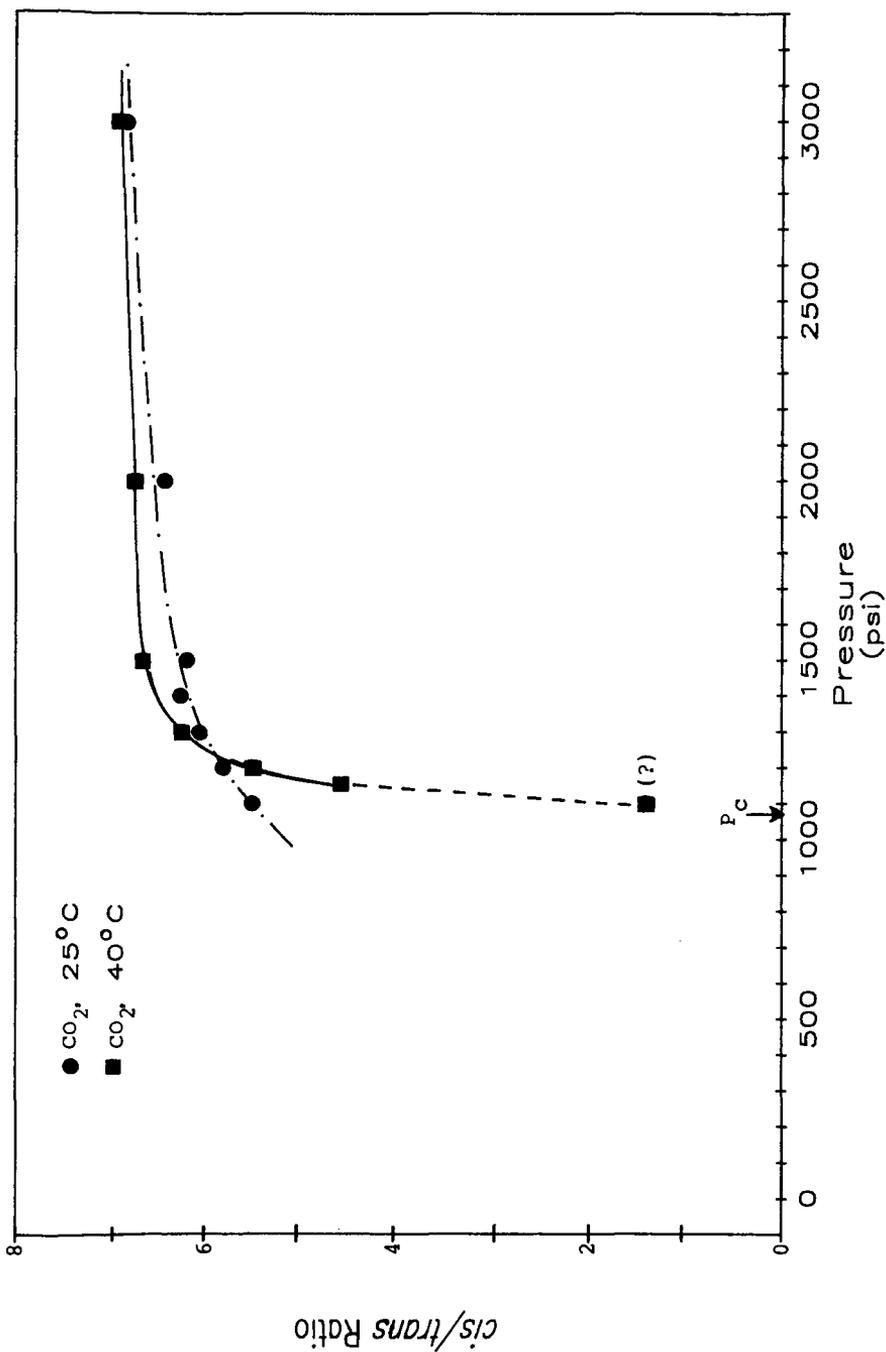


Figure 3. Pressure Effects in the Photoisomerization of trans-Stilbene.