Supercritical Fluids (SCFs) are currently used in several technological processes. One of the more interesting properties of SCFs as solvents is their high compressibility: most equilibrium and transport properties (solvation power, dielectric constant, viscosity, etc.) scale with the density and can be tuned near the critical point by modest changes of pressure and/or temperature.\(^1\) The high compressibility of SCFs near a critical point, coupled with attractive solvent-solute interactions, cause a local enhancement of solvent density around low-volatile solutes, a phenomenon usually referred to as critical clustering. There has been some debate about the characteristics of this solvation shell in the near-critical region, in particular about its strength and persistence against disruption. Several studies indicate that, in the critical vicinity, reaction products display a distinctive feature of condensed matter: a cage effect due to the enhanced local density.\(^2\)

In this work we examine the cage effect in SCFs by measuring the escape probability of 1-biphenyl-4-il-1-methyl-ethyl radicals, generated from the photolysis of (1-biphenyl-4-il-1-methyl-ethyl)-\textit{tert}-butyl diazene. The diazene compound is a relatively volatile solid, thermally stable up to 343 K, and dissolves in SCFs at densities below the critical value, allowing photoreaction experiments to be performed less than 2 K above \(T_c\). Results in CO\(_2\), Xe and Kr show that the escape probability, which is clearly a function of the solvent’s density, does not change significantly with the reduced temperature \(T_r\) in the near-critical region (\(T_r = T/T_c\) between 1.004 and 1.08). These results do not support the existence of enhanced cage effect due to critical fluctuations.