

KINETIC STUDIES OF BENZYL RADICALS IN SUPERCRITICAL FLUIDS

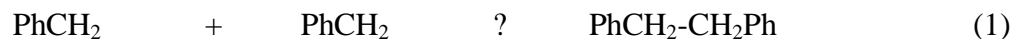
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The temperature and density dependent kinetics and mechanisms of the self-recombination reaction of benzyl radicals have been investigated in the gas to liquid transition range of solvent molecules of CO₂, Ar, N₂, He, Xe and CF₃H. Benzyl radicals were generated by UV laser photolysis, and time-resolved UV and FTIR spectroscopic techniques were used to monitor the kinetic behaviour of benzyl radicals over very wide pressure ranges (1-1000 bar) and temperatures (250-700 K) in optical high-pressure and high-temperature flow cells. With increasing solvent density and lowering temperature, the observed recombination rates increased, although the rate constants are already at the limiting high pressure value. We expect that this study would clarify what are properties characteristic to radical-solvent molecule complexes and how they influence on reaction kinetics of radicals depending upon the cluster size, mass, polarizability and dipole moment.

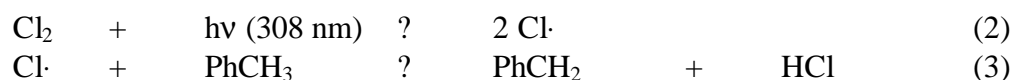
INTRODUCTION

Radical-molecule complexes have received considerable attention because of their role and impact on reaction mechanisms in supercritical fluids, for example, in density- and temperature-dependent radical association reactions [1] and diffusion-controlled kinetics [2]. Studies of pressure and temperature dependent rate constants of atom and radical recombination reactions provide useful experimental data to understand density dependent intermolecular interactions between radicals and solvent molecules from the gas phase to the supercritical state. Benzyl radicals were chosen as a prototype for large aromatic organic radicals. We present here current results of our on-going studies on pressure and temperature dependent kinetic studies of the recombination reaction of benzyl radical (PhCH₂) in supercritical fluids:



I - MATERIALS AND METHODS

Benzyl radicals were produced from the reaction of toluene with chlorine atom following the laser photolysis of molecular chlorine at 308 nm using an excimer laser:



Toluene (Aldrich, 99.8 % purity) and Cl₂ (MG, 99.998 % purity) were purified several times before use in a pump-freeze-thaw cycle. All other compressed gases were from MG, and impurities were removed by a gas cleaning adsorber (Oxisorb) and dust filters. Two high-

pressure and high-temperature optical flow cells were constructed to observe time-resolved UV and IR absorption signals and/or spectra of radicals of interest on time scales from nanoseconds to a few hundred microseconds.

II - RESULTS AND DISCUSSION

In the gas phase, the reaction rate constants reach a constant value, the so-called "limiting high pressure value", independent from the bath gas already at far below 1 bar. Very little temperature dependence on the limiting high pressure rate constants was observed. Our current results however clearly show that at higher pressures a further unexpected steady increase of the rate constants before they reach the diffusion-controlled regime, especially when strongly bound radical-CO₂ complexes are present and when temperature is lower. The diffusion rates of benzyl radicals in the medium density region of supercritical fluids also show much slower rates than predicted from the available semi-empirical diffusion coefficients for precursor molecules or benzyl radical itself, indicating further decreased diffusion rates of radicals in supercritical fluids due to the formation of radical-molecule complexes. Figure 1 illustrates these observations. Our experimental observation indicates that the importance of radical-solvent molecule complexes should be considered in studies of radical combination reaction kinetics in the medium density region of supercritical fluids.

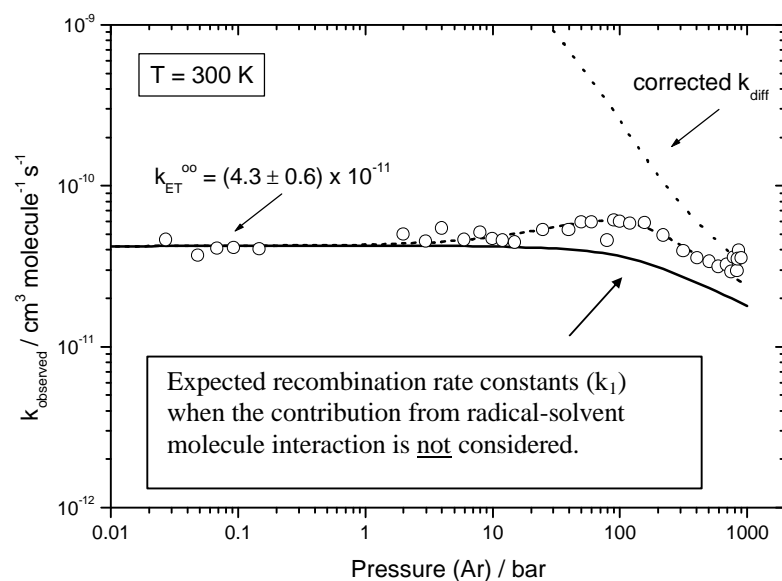


Figure 1. Observed recombination reaction rate constants of reaction (1) in Ar at 300 K. Experimental data with open circles; dotted line is the diffusion rate constant after correction; solid line as explained in the box.

ACKNOWLEDGEMENTS

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- [1] see for example, (a) Hippler, H., Schubert, V. and Troe, J., J. Chem. Phys., Vol. 81, **1984**, p.3931; (b) Luther, K., Oum, K. and Troe, J., J. Phys. Chem. A, Vol. 105, **2001**, p.5535
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