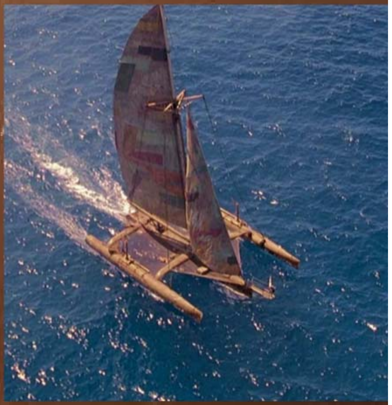
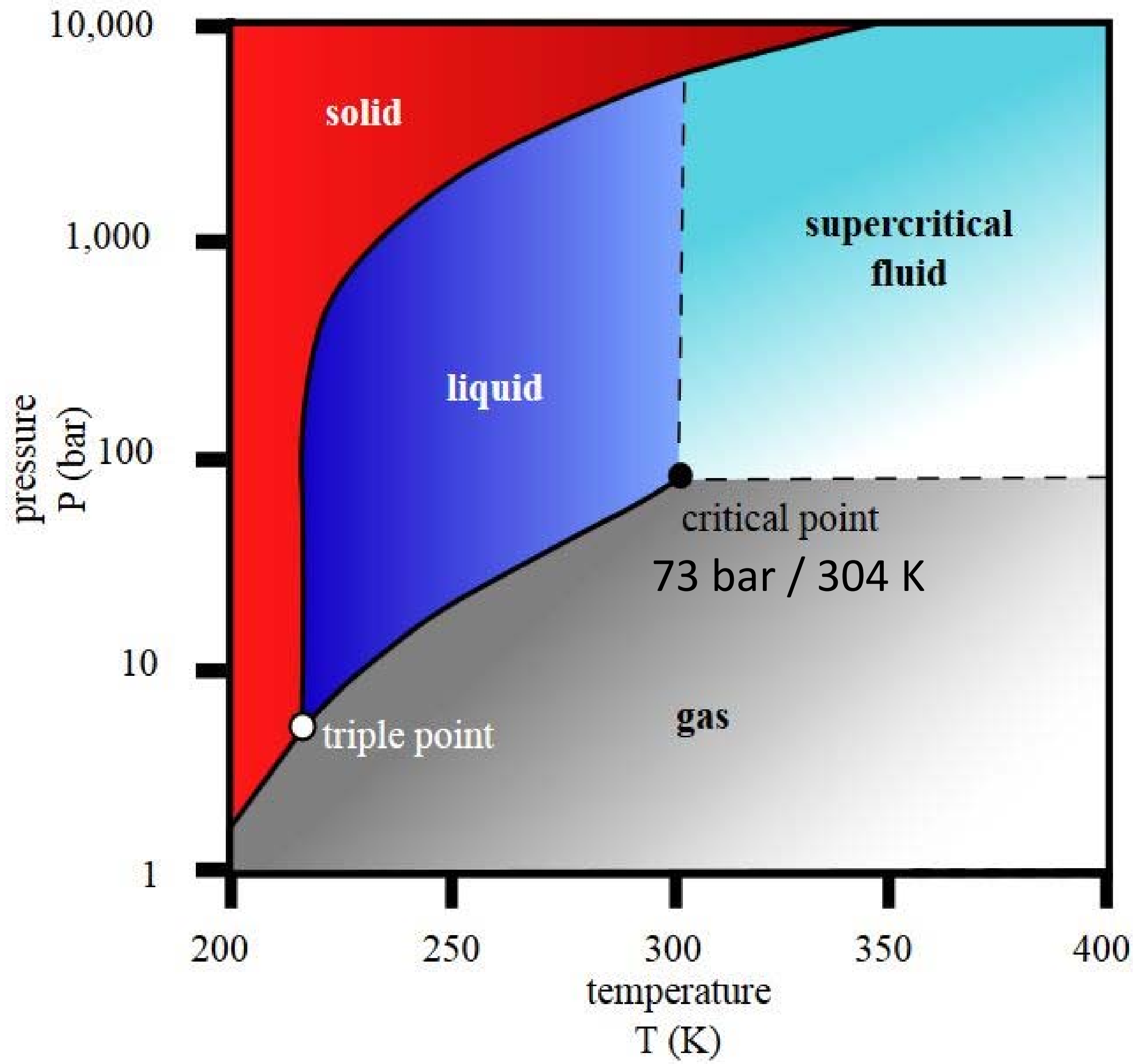


Escape from Waterworld: Chemistry in Hydrocarbons and Liquid and Supercritical Carbon Dioxide

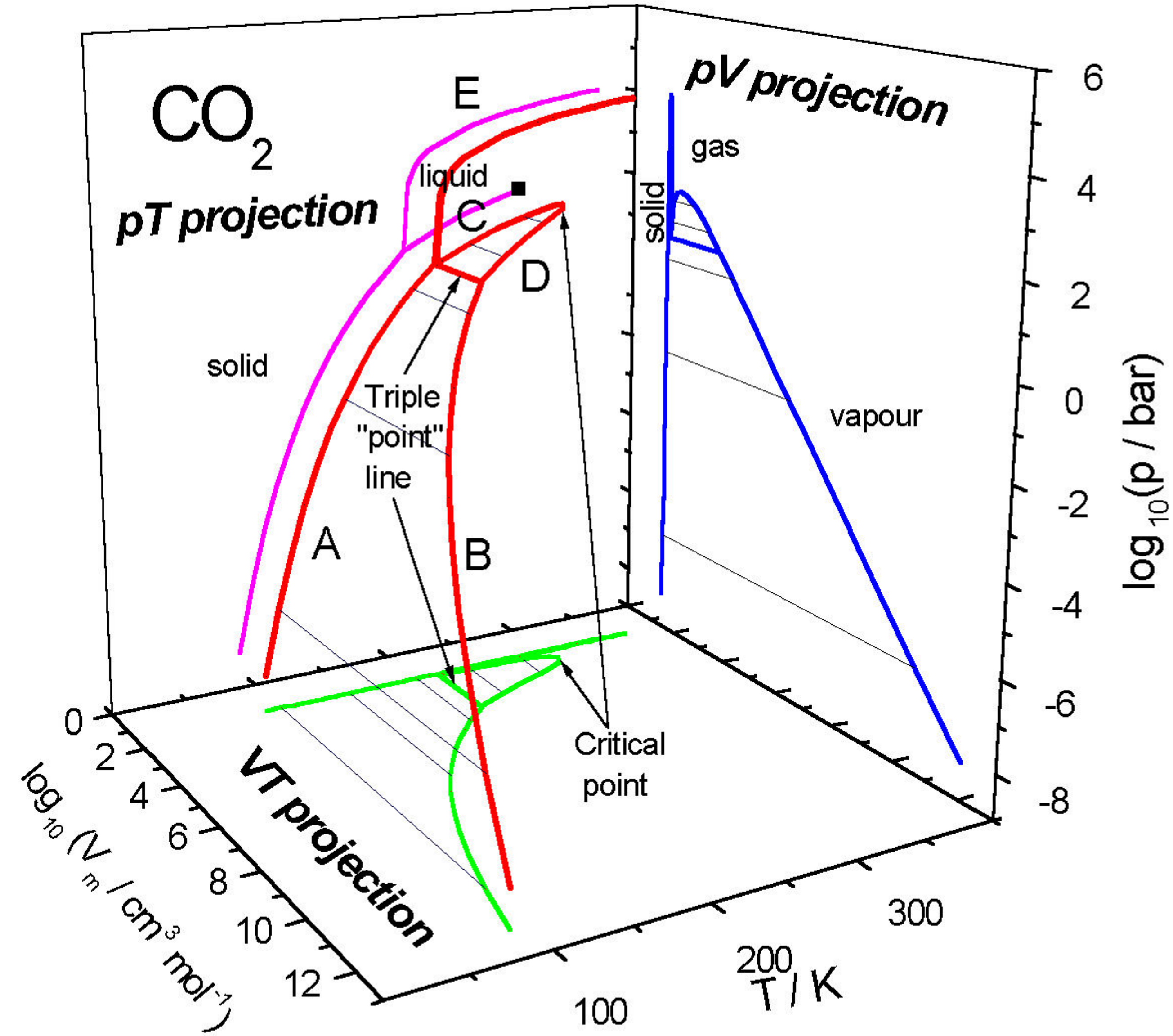
Robert Hodyss and Jack Beauchamp

Phase Diagram of Carbon Dioxide

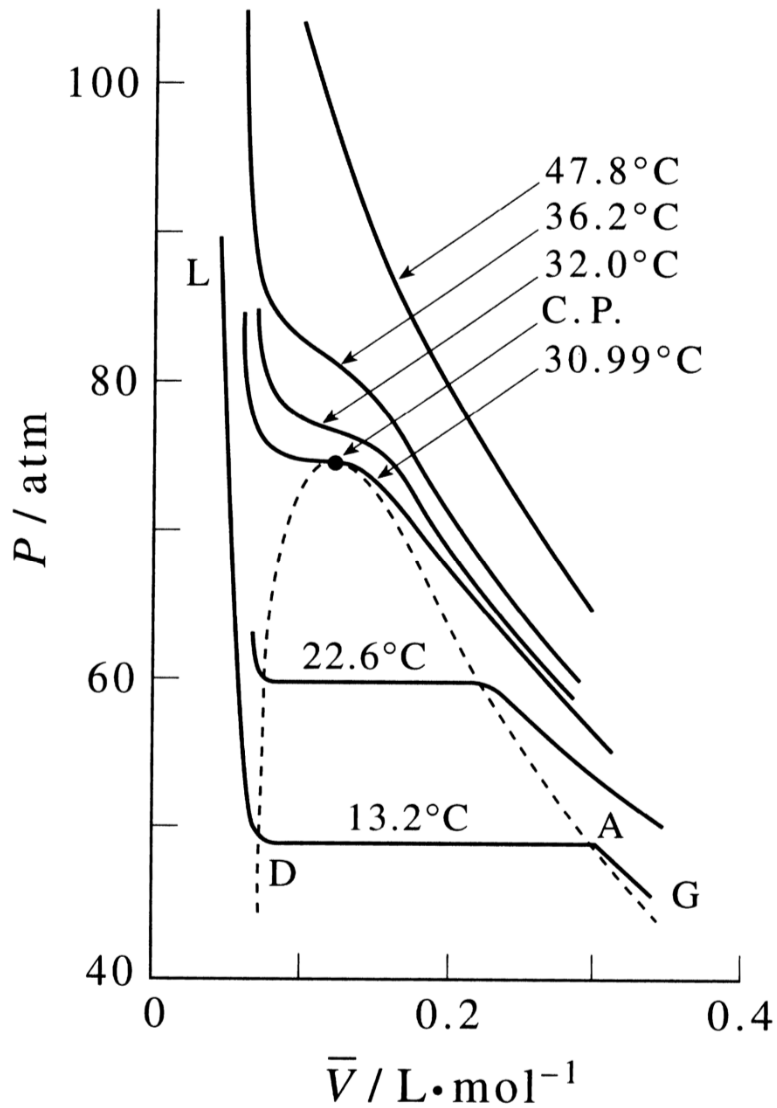


At pressures and temperatures above the critical point there is only a single phase.

3D Phase Diagram of Carbon Dioxide



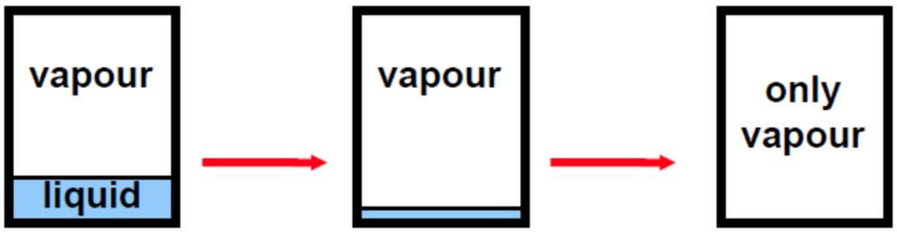
Isotherms for Carbon Dioxide
(P vs. V at constant T)



- Large V: ideal gas behavior.
- Only one phase above T_c.
- Dashed curve: liquid+gas coexist in this region.

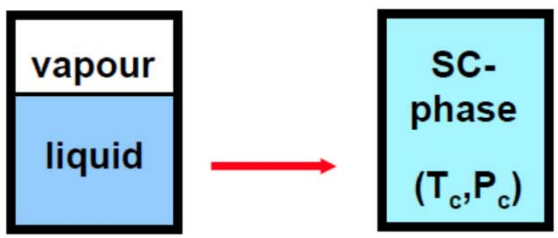
Carbon Dioxide PV Diagram (figure 16.7 McQuarrie and Simons, Physical Chemistry: A Molecular Approach)

1.)



The result of heating is the gas obeying to usual gas laws (for example Wan-der-Waals equation).

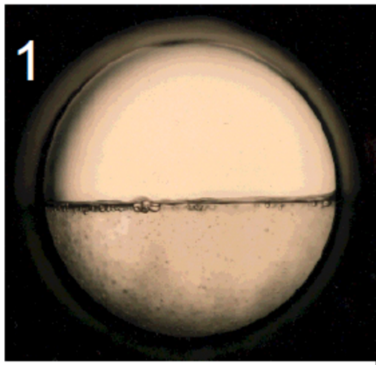
2.)



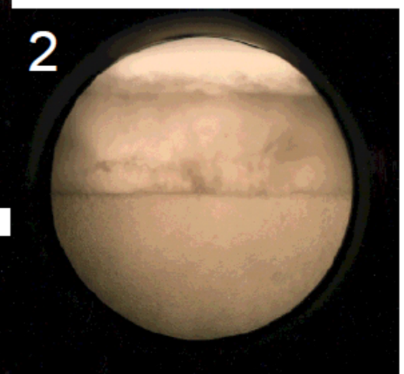
The result – new phase occurs so-called supercritical phase.

A supercritical fluid is a state where matter is compressible and behaves like a gas (i.e. it fills and takes the shape of its container), which is not the case when it is in a liquid state (an incompressible fluid that occupies the bottom of its container). However, a supercritical fluid has the typical density of a liquid and hence its characteristic dissolving power. That is why we cannot define the supercritical fluid as a liquid or as a gas.

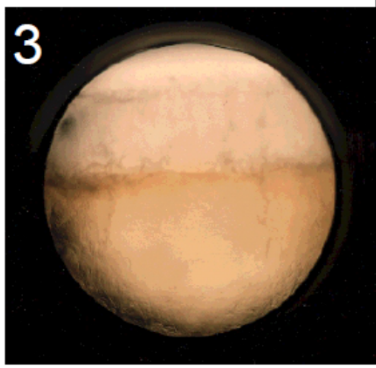
Transition of CO_2 Gas/Liquid Mixture to Supercritical Phase



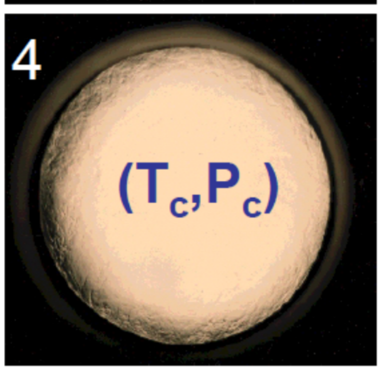
Here we can see the separate phases of carbon dioxide. The meniscus is easily observed.



With an increase in temperature the meniscus begins to diminish.



Increasing the temperature further causes the gas and liquid densities to become more similar. The meniscus is less easily observed but still exists.



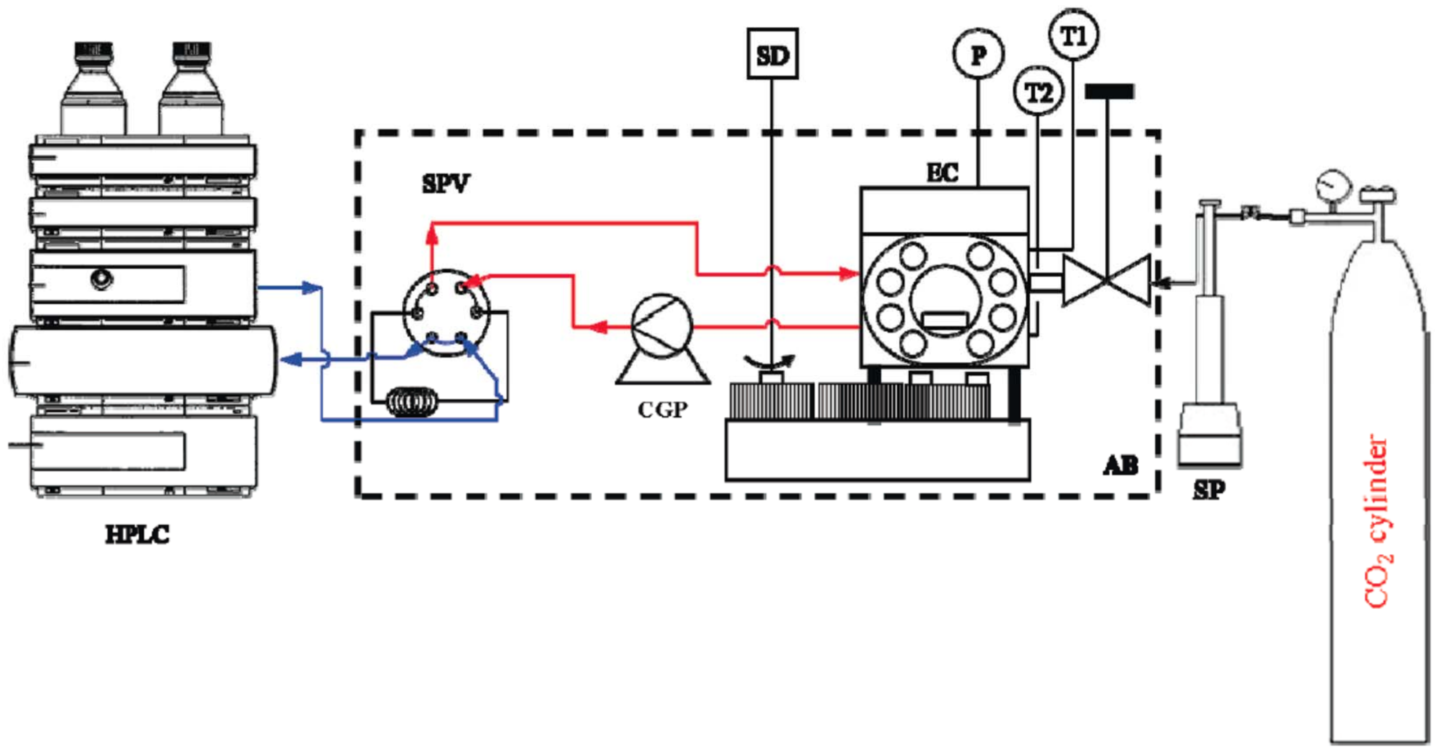
Once the critical temperature and pressure have been reached, the two distinct phases of liquid and gas are no longer visible. The meniscus can no longer be seen.
One homogenous phase called the "supercritical fluid" phase occurs.

https://www.google.com/#q=Muslim+Dvoyashkin+supercritical+carbon+dioxide

Critical points for different solvents

Compounds	Critical Temperature (°C)	Critical Pressure (atm)	Critical Density (g/ml)
Carbon Dioxide	31.3	72.9	0.448
Ammonia	132.4	112.5	0.235
Water	374.15	218.3	0.315
Nitrous Oxide	36.5	71.7	0.45
Xenon	16.6	57.6	0.118
Krypton	-63.8	54.3	0.091
Methane	-82.1	45.8	0.2
Ethane	32.28	48.1	0.203
Ethylene	9.21	49.7	0.218
Propane	96.67	41.9	0.217
Pentane	196.6	33.3	0.232
Methanol	240.5	78.9	0.272

Measurements of Solubilities in Supercritical CO_2



Apparatus for measuring solubility in both liquid and supercritical CO_2. The solution is mixed and equilibrated in “EC”(equilibration chamber), sampled through a valve (“SPV”) with a filtration frit, and quantified by liquid chromatography (HPLC).

Elizalde-Solis, O., and Galicia-Luna, L.A. (2011). New apparatus for solubility measurements of solids in carbon dioxide. *Ind. Eng. Chem. Res*. 50:207–202. doi:10.1021/ie1009537

Measurements of Solubilities in Supercritical CO_2

Conclusions from examining a wide range of molecular species

Carbon dioxide exhibits properties typical of hydrocarbon solvents, such as toluene; however, for basic molecules, such as pyrrole, $C0_2$ provides more H bonding basicity than do hydrocarbon solvents. No significant difference in polarity can be detected between the liquid and supercritical phases. This view of $C0_2$ as a "hydrocarbon" solvent with unusual properties (infinite compressibility in the supercritical state, low surface tension and viscosity, low polarizability, and ease of solute recovery) will lead to additional exploration of its utility in chemistry.

Perusal of the literature suggests that almost anything can be dissolved in $scCO_2$, sometimes with the help of a co-solvent or complexing agent, including enzymes with retained activity, and as a last resort, using an inverse micelle.

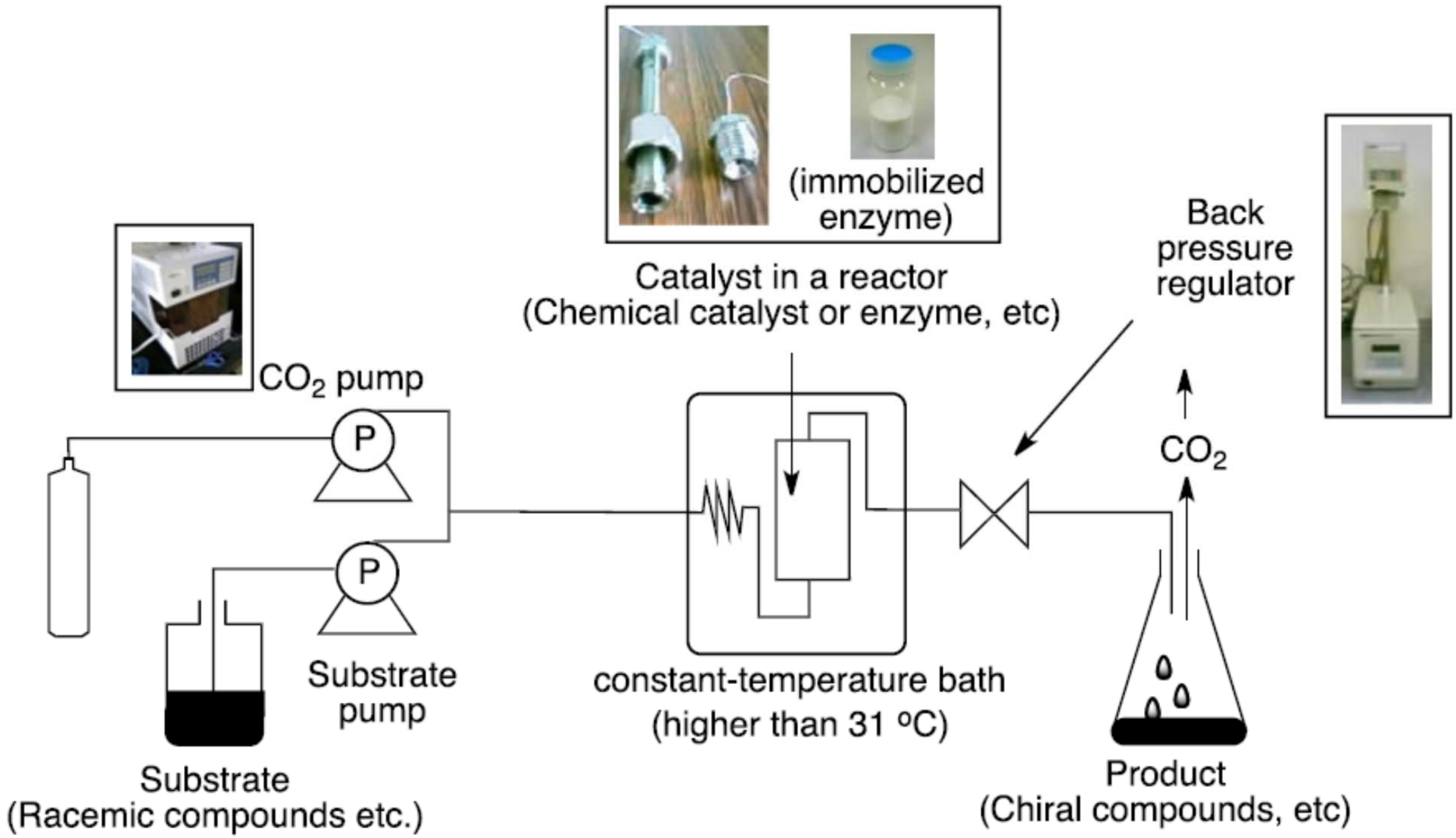
Comparison of Properties of Gases, Liquids, and Supercritical Fluids

Order of density, viscosity and diffusivity of gases, liquids and supercritical fluids.

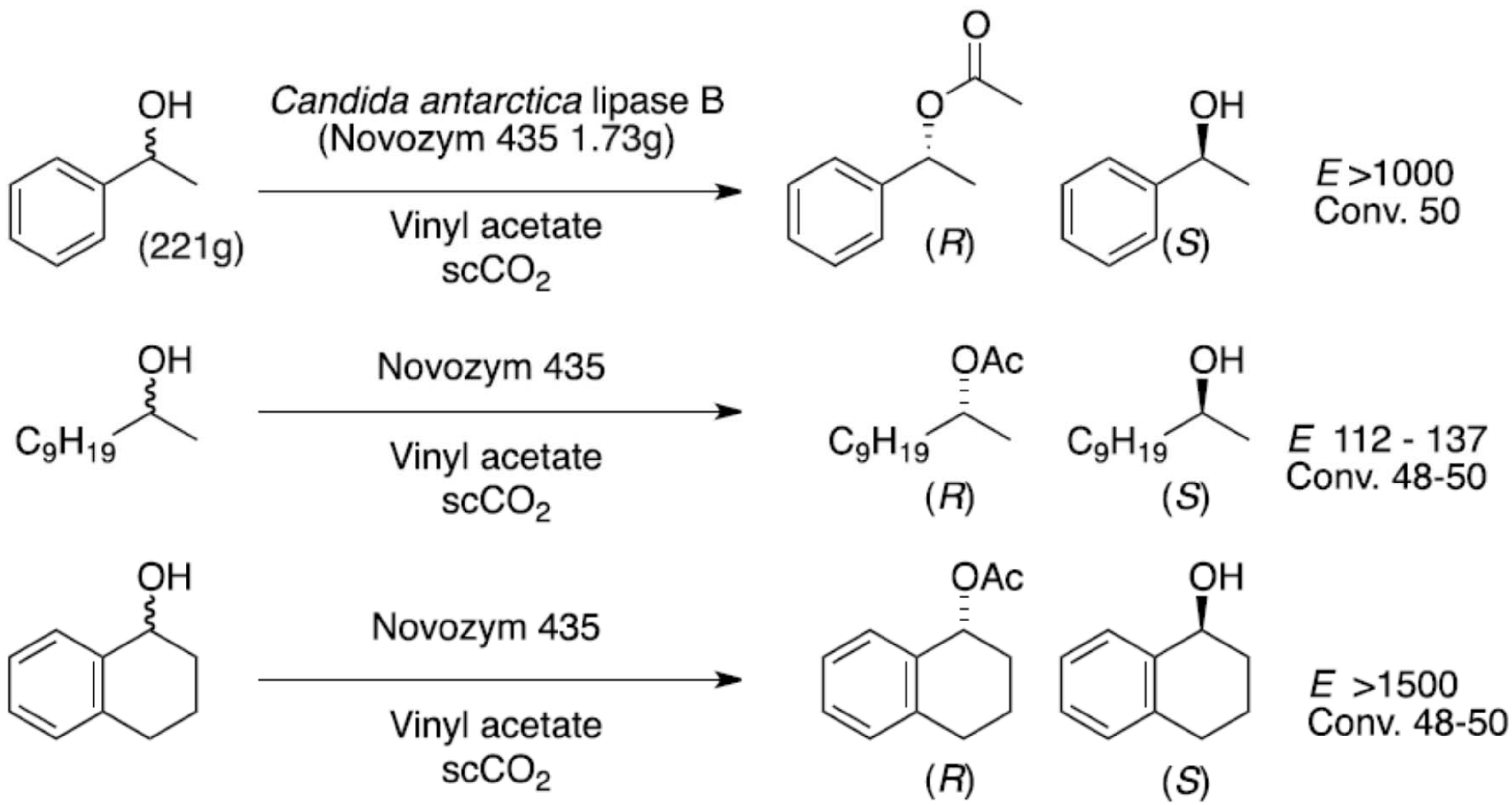
Physical state	Density (g/ml)	Viscosity (g/cm x s)	Diffusivity (cm^2/s)
Gas	10^{-3}	10^{-4}	10^{-1}
Liquid	1	10^{-2}	10^{-6}
Supercritical fluid	0.2-0.9	10^{-4}	10^{-3}

Continuous lipase-catalyzed kinetic resolution of alcohols using $scCO_2$-flow reactor

Matsuda, T. Recent progress in biocatalysis using supercritical carbon dioxide. *J. Biosci. Bioeng.* **2013**, *115*, 233–241



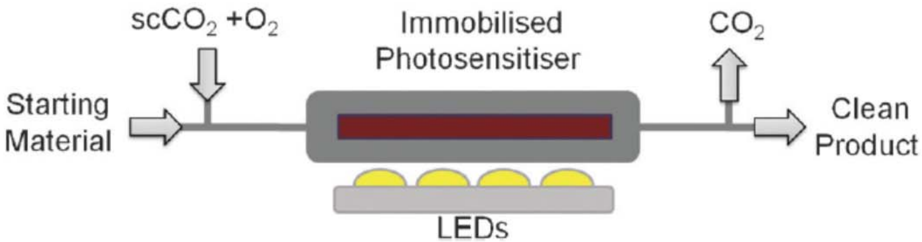
NO ORGANIC SOLVENT USED FOR SYNTHESIS OF CHIRAL COMPOUNDS



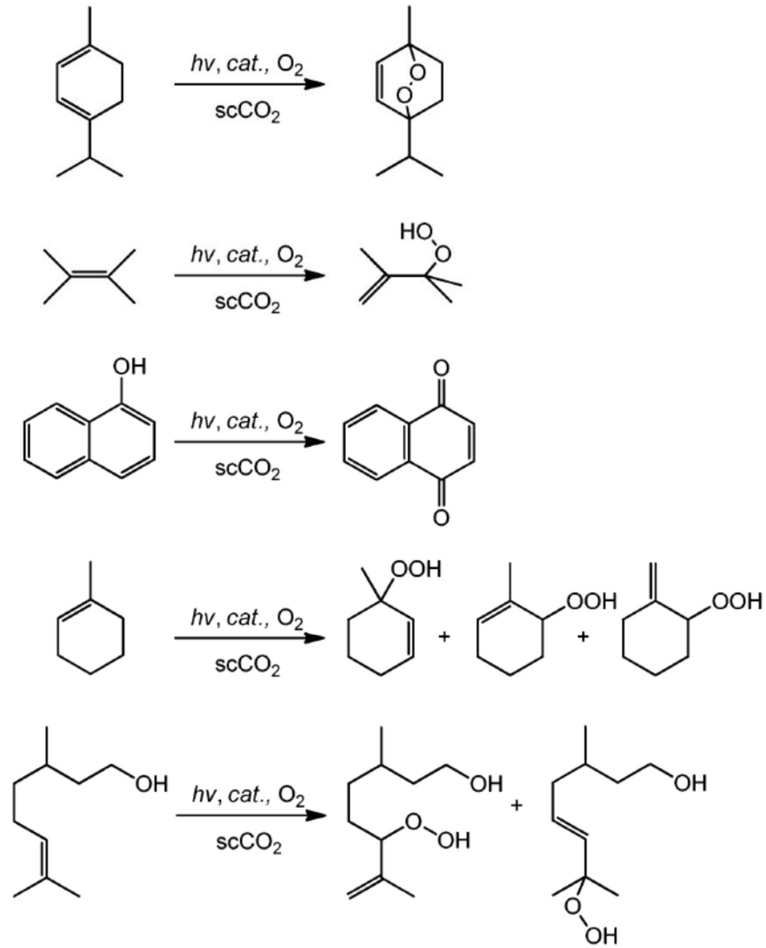
Matsuda, T. Recent progress in biocatalysis using supercritical carbon dioxide. *J. Biosci. Bioeng.* **2013**, *115*, 233–241

Immobilized photosensitizers for continuous flow reactions of singlet oxygen in supercritical carbon dioxide

X. Han, R. A. Bourne, M. Poliakoff and M. W. George, Chem. Sci., 2011, 2, 1059–1067



Schematic of the continuous photo-oxidation apparatus using immobilized photocatalysts in $scCO_2$.

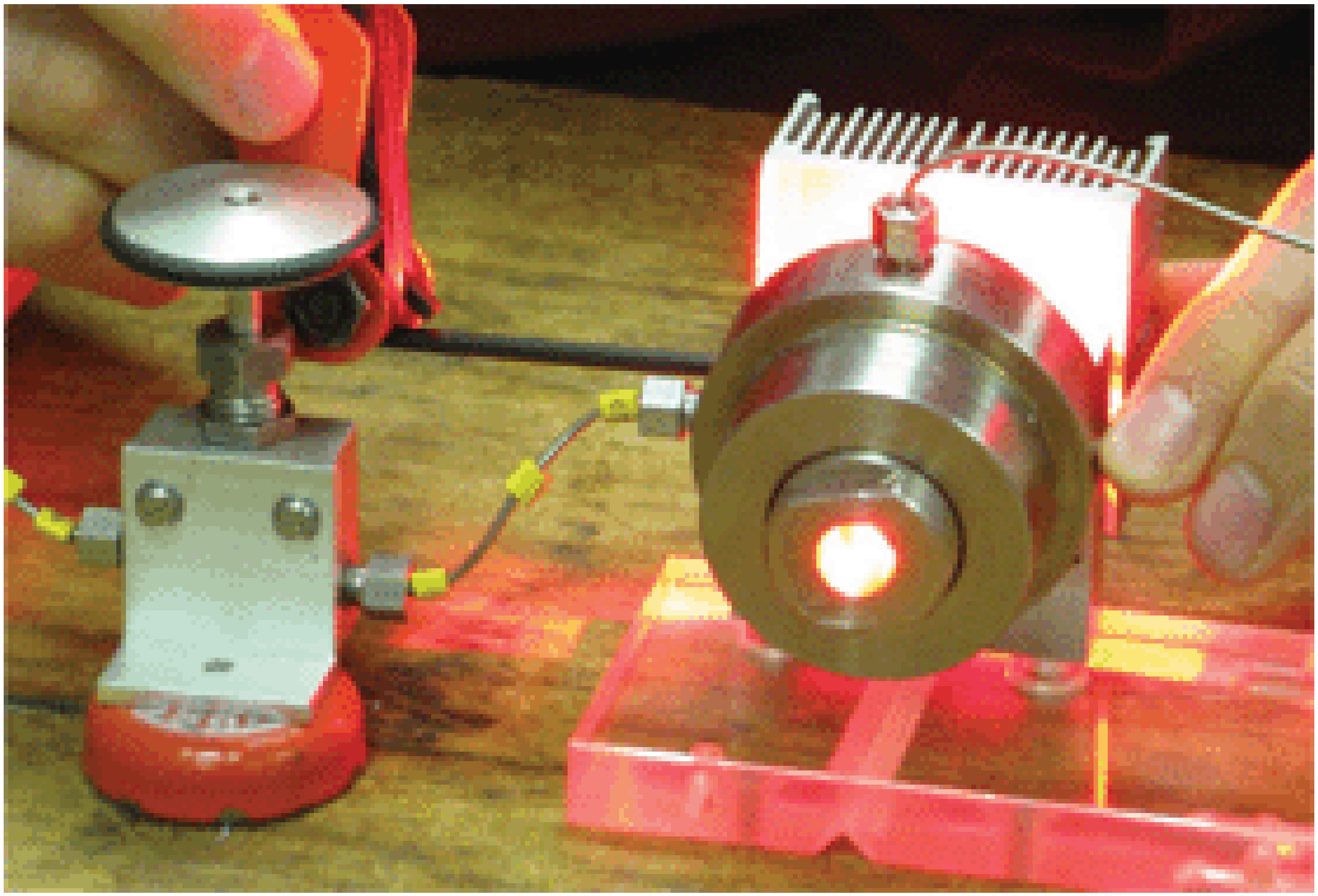


Because of the full miscibility of $scCO_2$ with permanent gases, such as H_2 and O_2, and its ability to dissolve organic compounds, especially with the aid of co-solvent, single phase reaction mixtures often show exceedingly high rates that are rarely achievable in conventional liquid solvents due to inherent gas-liquid mass transport limitations.

Han, X. and Poliakoff, M.: Continuous reactions in supercritical carbon dioxide: problems, solutions and possible ways forward, Chem. Soc. Rev., 41, 1428e1436 (2012).

Immobilized photosensitizers for continuous flow reactions of singlet oxygen in supercritical carbon dioxide

X. Han, R. A. Bourne, M. Poliakoff and M. W. George, Chem. Sci., 2011, 2, 1059–1067



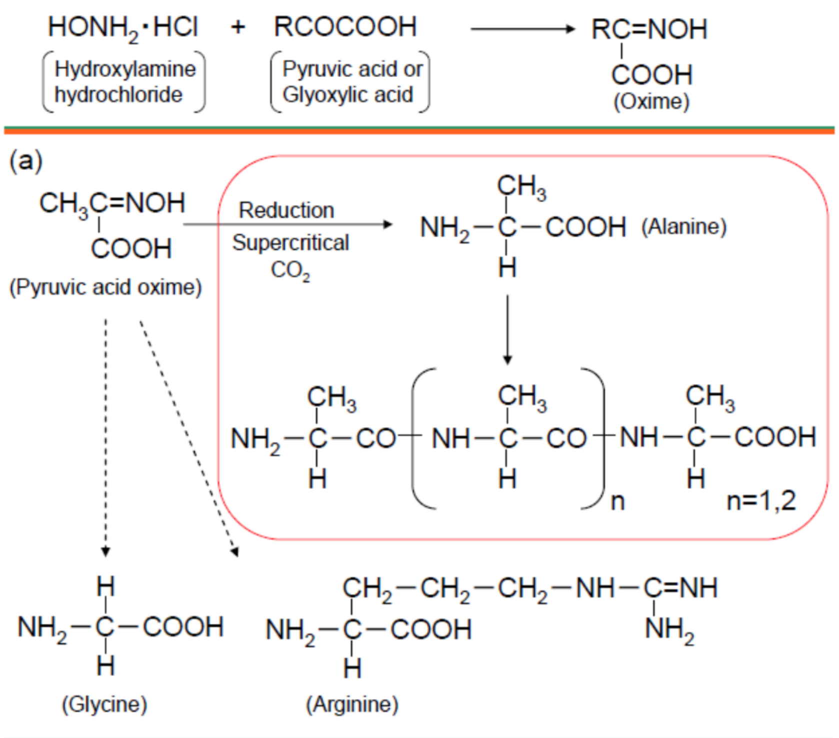
Amino Acid and Peptide Synthesis in a Supercritical Carbon Dioxide - Water System

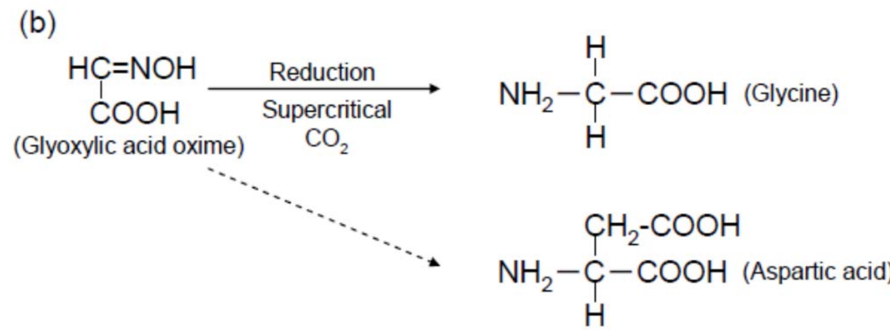
Kouki Fujioka, Yasuhiro Futamura , Tomoo Shiohara, Akiyoshi Hoshino, Fumihide Kanaya, Yoshinobu Manome and Kenji Yamamoto

Int. J. Mol. Sci. **2009**, *10*, 2722-2732; doi:10.3390/ijms10062722

Using a supercritical CO_2/liquid H_2O (10:1) system which mimicked crustal soda fountains, production of amino acids from hydroxylamine (nitrogen source) and keto acids (oxylic acid sources) is demonstrated. In this research, several amino acids were detected with an amino acid analyzer. Moreover, alanine polymers were detected with LC-MS, indicating that amide bond formation occurs to yield peptides.

Amino Acid and Peptide Synthesis in a Supercritical Carbon Dioxide - Water System

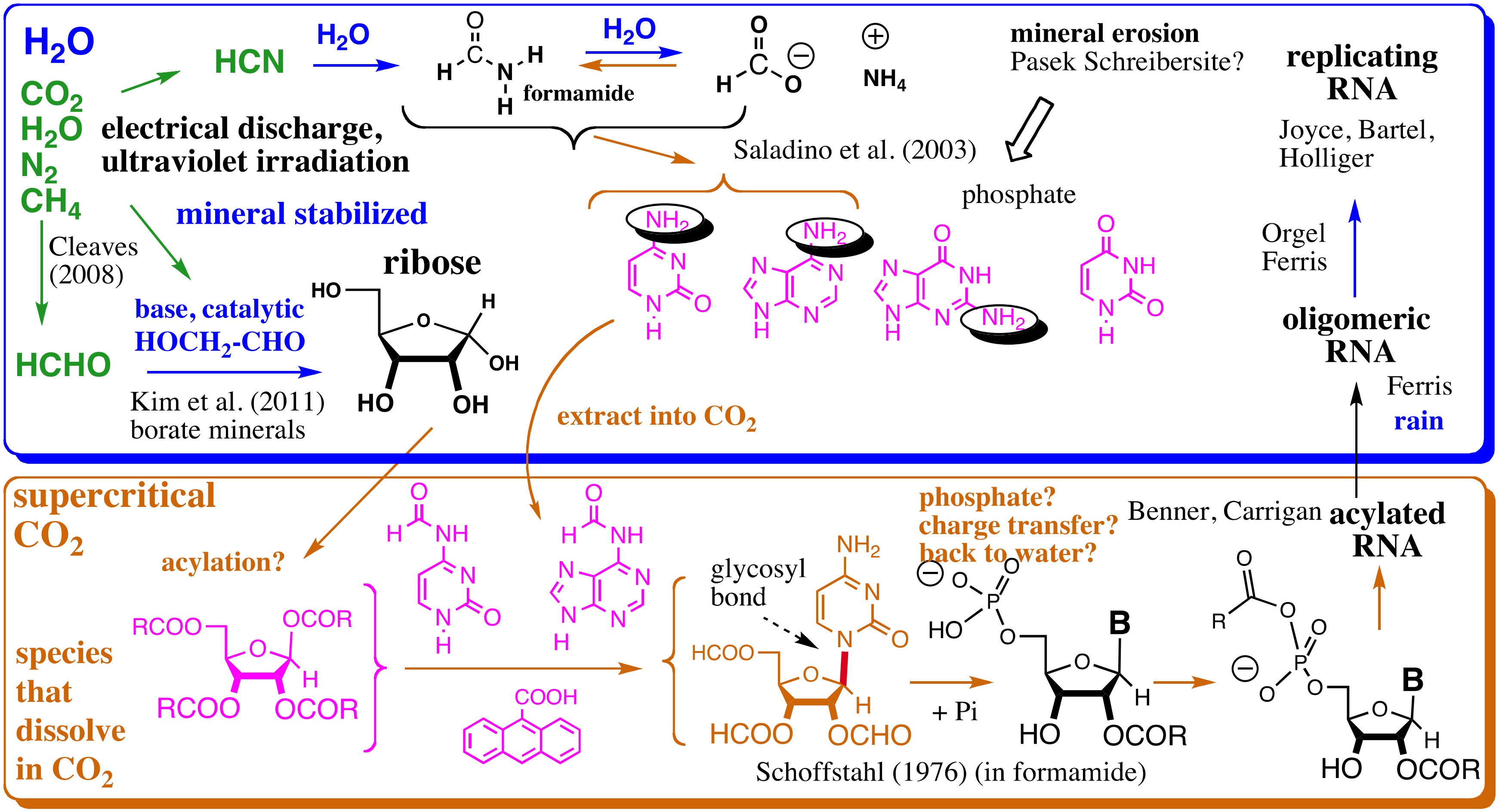




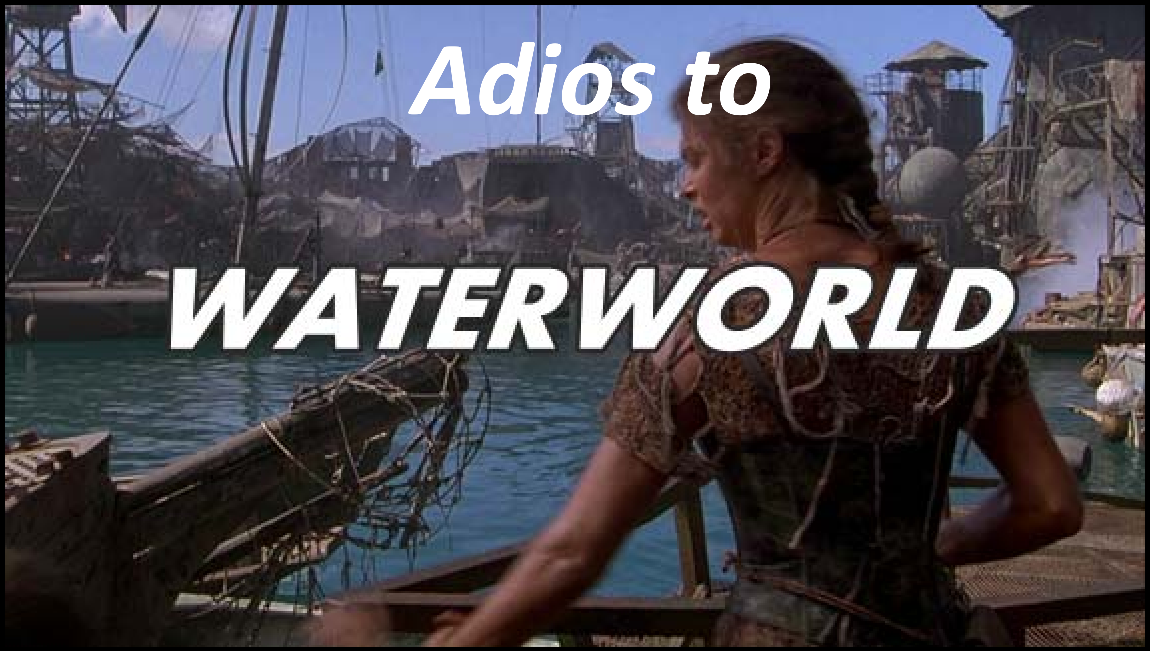
Is supercritical CO_2 likely to be important in the origin of an RNA world?

In preliminary studies (magenta coloring in following slide), Steve Benner and coworkers showed that all RNA nucleobases are soluble in $scCO_2$, some to a considerable extent. Further, acylated nucleobases are soluble; these are potentially important in models of RNA formation that involve electrophilic solvents (e.g., formamide). With the exception of uracil, where the partition between $scCO_2$ and water is close to unity, the partition between water and $scCO_2$ of the other nucleobases strongly favors $scCO_2$. Accordingly, no matter where they are formed, should these species be present in a planetary environment where $scCO_2$ and water are in contact/equilibrium, *these preliminary studies show that nucleobases will be extracted into the $scCO_2$ phase*. ***Thus $scCO_2$ appears to offer an "organics-friendly" environment to enrich and fractionate bioorganic materials on a planetary scale.***

Is supercritical CO_2 likely to be important in the origin of an RNA world? Steve Benner is Optimistic!



Key: in the atmosphere in aquifer in supercritical CO_2 works in $scCO_2$ (Benner preliminary studies)



… with apologies to Kevin Costner

Waterworld: Also known as the biggest box office flop of all time. This film sets Kevin Costner in a dystopian future where the sea levels have risen so much that all of earth is covered in water. Released in 1995 this was the most expensive film ever produced at the time, and recouped only about half of its $175 million budget at the box office. Also of note, is that this film introduced the issue of global warming well before it was on the national stage. This is an epic tale of a lone mariner setting out to save the life of a child and discover the last vestiges of dry land. It's a well-made film even if the characters are some what one-dimensional. (Review by "French Toast Sunday"; ranked as one of top six best disaster films)