GREEN CHEMISTRY

SEMESTER-VI
DSE-A3

Dr. Kalyan Kumar Mandal
Associate Professor
Department of Chemistry
St. Paul's C. M. College
Kolkata

Contents

Green Solvents

From the purpose of greenness and sustainability, use of volatile organic compounds (VOCs) as solvent should be avoided. This is because:

(1) Many organic solvents with high vapour pressures lead to chemical hazards including high inflammability, low flash points, toxicity, carcinogenicity and environmental pollution, etc. These cause major health effects, such as, damage of the nervous system, damage of kidney and liver system, cancer, etc.

(1) These cause major health effects, such as, damage of the nervous system, damage of kidney and liver system, cancer, etc.

However, alcohols and alkanes (e.g., hexane, heptane, etc.) are less harmful than the halogenated solvents like chloroform ($CHCl_3$), methylene chloride (CH_2Cl_2), carbon tetrachloride (CCl_4), acetonitrile (MeCN), tetrahydrofuran (THF), benzene, etc.

Green Solvents

Green solvents:

The solvents which are not harmful to human health and the environment are called green solvents.

Example:

Supercritical fluids (H_2O, CO_2), ionic liquids, polyethylene glycol

Criteriaof green solvents:

- Low vapour pressure
- High boiling point
- Non-toxic and carcinogenic
- Non-volatility
- Non-flammability
- Good dissolving agent
- Recyclability

Pfizer Solvent Selection Guide

Greenness of the solvent

Undesirable solvent	Usable solvent	Preferred solvent
Pentane	Cyclohexane	Water
Hexane	Toluene	Acetone
Diethyl ether	TBME	Ethanol
Methylene chloride (DCM; CH_2Cl_2)	Isooctane	2-Propanol
Chloroform ($CHCl_3$)	Acetonitrile	1-Propanol
Dimethylformamide (DMF)	THF	Heptane
Pyridine	2-MeTHF	Ethyl acetate
Dioxane	Xylenes	Isopropyl acetate
Dimethoxyethane (DME)	DMSO	Methanol
Benzene	Acetic acid	Ethyl methyl ketone
Carbon tetrachloride	Ethylene glycol	1-Butanol
		t-Butanol

Greenness of the solvent increases →

Solvent Replacement Table

Solvent replacement table

Undesirable Solvent(s)	Alternative(s)
Pentane, Hexane	Heptane
Diethyl ether, Di-isopropyl ether	2-Me-THF or *t*-Butyl methyl ether
Dioxane, Dimethoxyethane	2-Me-THF or *t*-Butyl methyl ether
Chloroform, Dichloroethane, Carbon tetrachloride	Dichloromethane
Dimethyl formamide, Dimethylacetamide	Acetonitrile
Pyridine	Triethylamine
Dichloromethane (chromatography)	Ethyl acetate
Benzene	Toluene

Supercritical Fluids (SCFs)

Supercritical Fluids: It is a substance at a temperature and pressure higher than its critical point where distinct liquid and vapour phases do not exist.

Properties

(1) It exhibits particular properties and has an intermediate behavior that of a liquid and a gas.

(2) It possess liquid like densities, gas like viscosities and diffusivities intermediate to that of a liquid and a gas.

Physical properties of gas, supercritical fluids and liquids

Properties	Gas	Supercritical fluid	Liquid
Density (g ml^{-1})	$(0.6\text{-}2) \times 10^{-3}$	0.2-0.5	0.6-1.6
Viscosity (g cm^{-1} s^{-1})	$(1\text{-}3) \times 10^{-4}$	$(1\text{-}3) \times 10^{-4}$	$(0.2\text{-}3) \times 10^{-2}$
Diffusion coefficient (g cm^{-1} s^{-1})	$(1\text{-}4) \times 10^{-1}$	10^{-3} - 10^{-4}	$(0.2\text{-}2) \times 10^{5}$

Supercritical Fluids (SCFs)

Examples:

(1) Supercritical water and carbon dioxide

(2) Methanol, ethanol, ethane and propane are also used in their supercritical phase for different chemical processes such as extraction, chemical reactions, toxicity removal, dye degradation, etc.

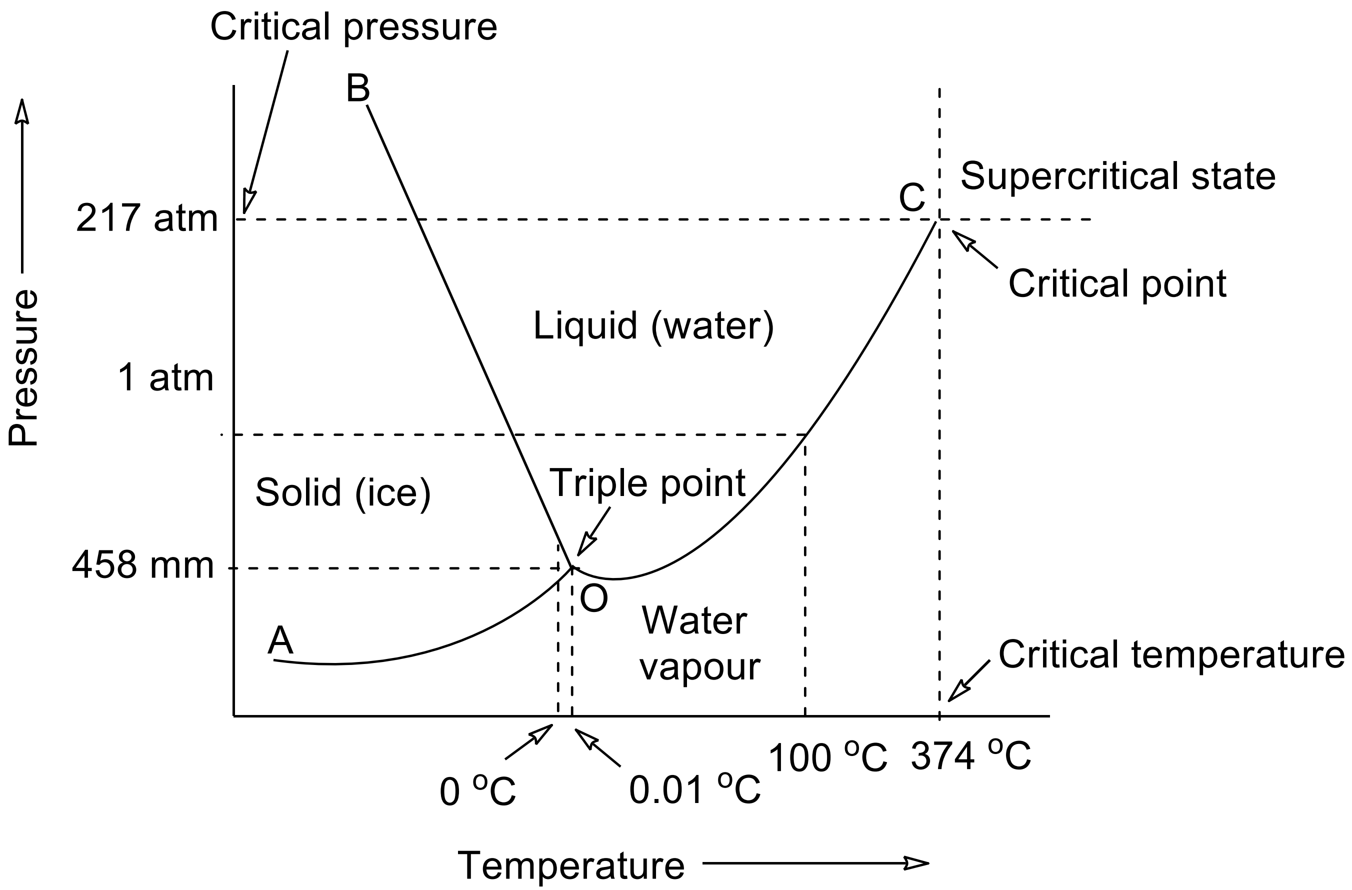
Advantages:

They are:

- chemically stable
- non-toxic
- non-flammable
- non-volatile
- less costly
- easily recylable and reusable
- obtained in highly purified forms
- more solvating than the conventional organic solvents

Supercritical Water (SCW)

Supercritical water



Supercritical Water (SCW)

- Water can exist in three forms - liquid, solid and vapour depending on the temperature and pressure.
- The point 'O' in the phase diagram indicates the 'triple point' of water. At this point, all the three phases (liquid, vapour and solid) of water co-exist.
- The temperature and pressure of triple point of water are 0.01 ^{o}C and 458 mm.
- The area AOB, BOC and AOC (right side) indicate solid, liquid and vapour phases of water, respectively.
- Point 'C' in the phase diagram is known as the critical point. The critical temperature and critical pressure of water rae 374 ^{o}C and 217 atm, respectively.
- Therefore, water cannot remain in the liquid state above 374 ^{o}C (critical temperature) and 217 atm (critical pressure).

Critical point: This is the highest temperature and pressure at which a pure substance can exist in vapor/liquid equilibrium. At temperatures higher than the critical temperature, the substance can not exist as a liquid, no matter what the pressure.

Supercritical Water (SCW)

- Super critical water refers to a state of water where temperature and pressure are above its critical temperature (374 ^oC) and critical pressure (217 atm). In this state, vapour and liquid phases of water do not exist and at this state water has the properties in between the true liquid and true vapour.

- The properties of supercritical water can be changed by varying the temperature and pressure. When the pressure is relatively less, then supercritical water possesses the vapour-like properties and when the pressure is very high, then the supercritical water possesses the liquid-like properties.

- The physical properties such as viscocity, density, dielectric constant, hydrogen bonding and ionic product are remarkably different from the normal water.

Supercritical Water (SCW)

Properties of Supercritical water

Density: Its density is about one-third of water at normal state. It has a density between that of water vapour and liquid at standard conditions.

Dielectric constant: It has low dieelctric constant than normal water and the dielectric constant is reduced to 2-30 from 87.7 9 at 0 ^{o}C for normal water). Due to low dielectric constant, it behaves much less like polar solvent and hence non-polar substances like organic compounds and oxygen are strongly soluble in SCW systems. Thus, SCW can be used an excellent medium for organic substances and oxygen.

Viscosity: Viscosity of SCW is lower than that of normal water.

Ionic product: Ion product is about 1000 times that of water at room temperature.

- The ion product reaches its maximum around 250 °C and its temperature gradually increases as the pressure increases. At higher temperatures, the ion product decreases rapidly due to density decrease, approaching gas-like properties.
- The larger ion product indicates that the acidic and/or alkaline properties become stronger.

Supercritical Water (SCW)

Uses of supercritical water

(1) Used as medium in supercritical water oxidation (SCWO):

(i) SCWO is an effective and advanced oxidation technology to destruct organic matters.

(ii) In the presence of SCW, organic wastes are throughly oxidised and decomposed into harmless substances like N_2, CO_2, etc., under excess oxidants in single phase.

(2) Used for biomass abd waste conversion for production of renewable hydrogen: In SCW (in absence of added oxidants), organics present in biomass and waste are converted into fuel gases and are easily separated from the water phase by cooling to ambient temperature. The produced high-pressure gas contains maximum renewable hydrogen gas.

(3) Used for nuclear power generation

(4) Used as solvent for decaffeination of coffee beans, tea leaves, and other caffeine-containing materials

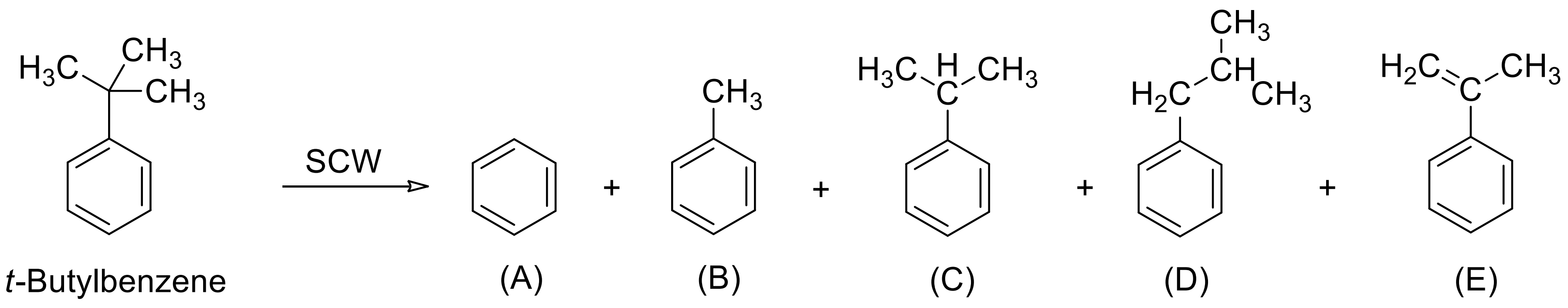
(5) Used for production of super methanol by reforming of crude glycerine

(6) Used for production of biofuels via hydrothermal conversion

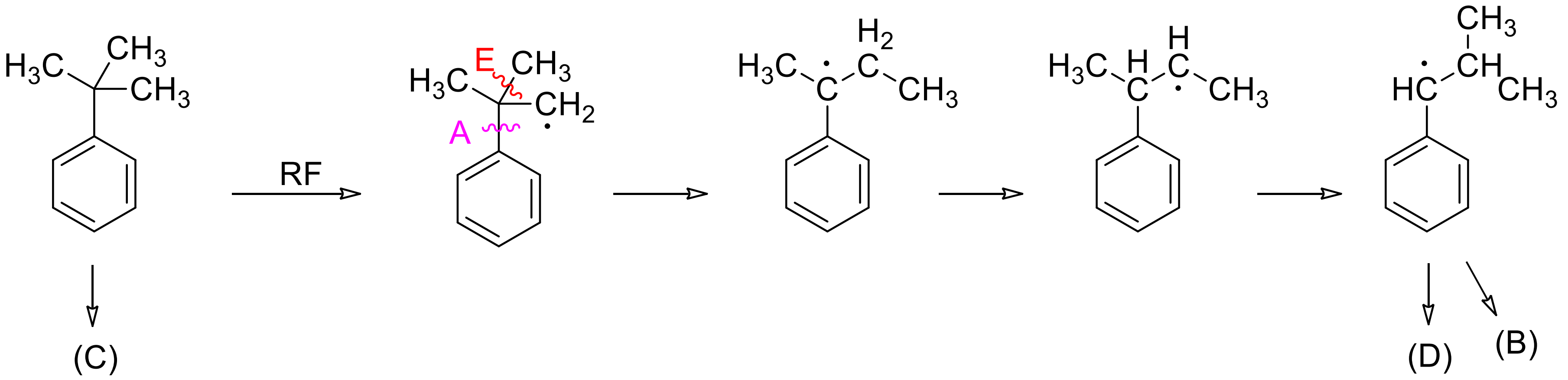
Reaction in Supercritical Water

(1) Pyrolysis of *t*-butylbenzene

The side chain of an aromatic hydrocarbon degrade in SCW through radical mechanism. The product mixture contains benzene (A), toluene (B), cumene (C), isobutylbenzene (D) and 2-phenylpropene (E).



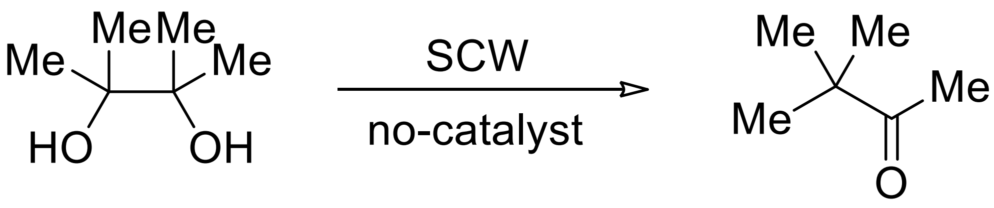
- The transformation occurs by radical formation by transfer reaction followed ny radical termination reaction.



Reaction in Supercritical Water

(2) Pincol-pinacolone rearrangement

- A non-catalytic pinacol-pinacolone rearrangement is performed in the near-critical region in SCW.
- The reaction shows excellent performance with respect to catalytic process when it is carried out in strong acids.
- The use of large amount of catalyst is avoided in SCW method.
- In conventional method, strong monobaic acids are used as catalysts and it the main drawback in the context of green sysnthesis.

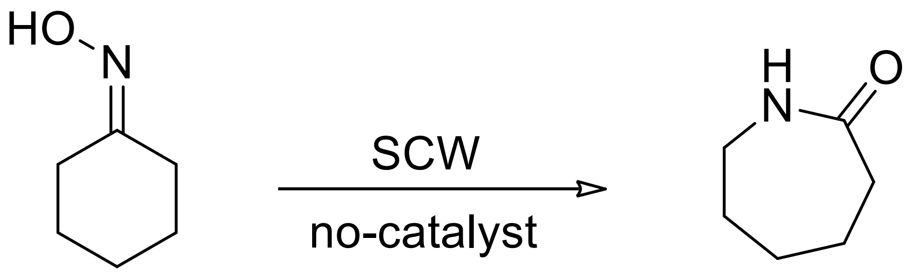


Pinacol Pinacolone

Reaction in Supercritical Water

(3) Beckmann rearrangement

- In the conventional method, high concentration of protic or Lewis acid is commonly used.
- The conversion of cyclohexanone oxime into ε-caprolactam can be achieved in the near-critical region in SCW.
- Here, the rearrangement is carried out under acid free conditions.

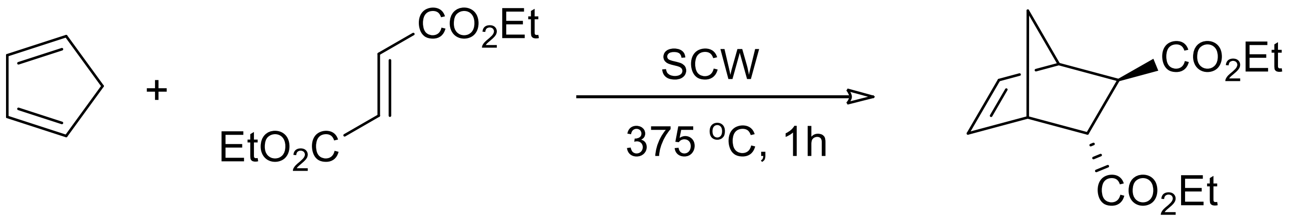


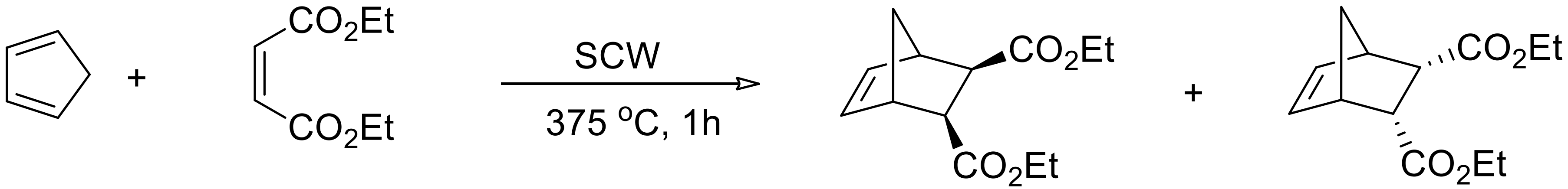
Cyclohexanone oxime ε-Caprolactam

Reaction in Supercritical Water

(4) Diels-Alder reaction

- In Diels-Alder reactions, the reagents used show a tendency to polymerize on heating and results soilidification inside the reaction vessel.
- High temperature is required to resolve the problem which is problematic in conventional heating in normal water.
- The Diels-Alder reactions in SCW can overcome all these problems and give products in high yields.

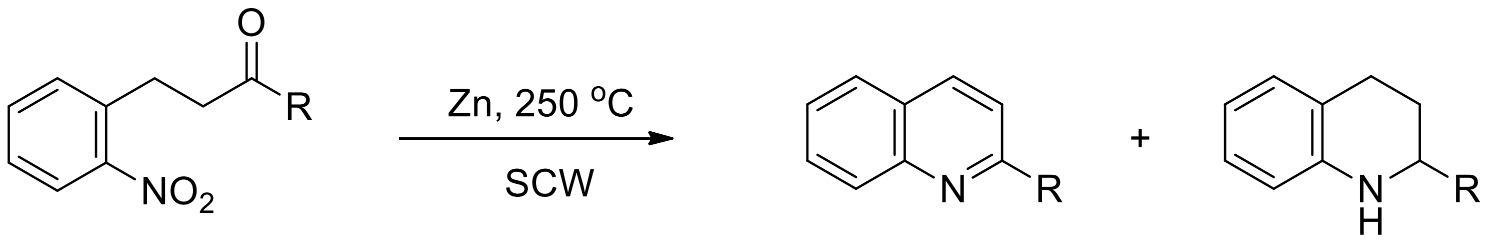




Reaction in Supercritical Water

(5) Reduction of aromatic nitro compounds

- Nitrobenzene containing different substituents is reduced to the corresponding aniline derivatives by Zn in SCW to give reduced product in 90-90% yield.
- Under this condition, Zn reacts with water and produces hydrogen which helps to reduce the nitro group.



R = H	97	3
R = Me	65	35