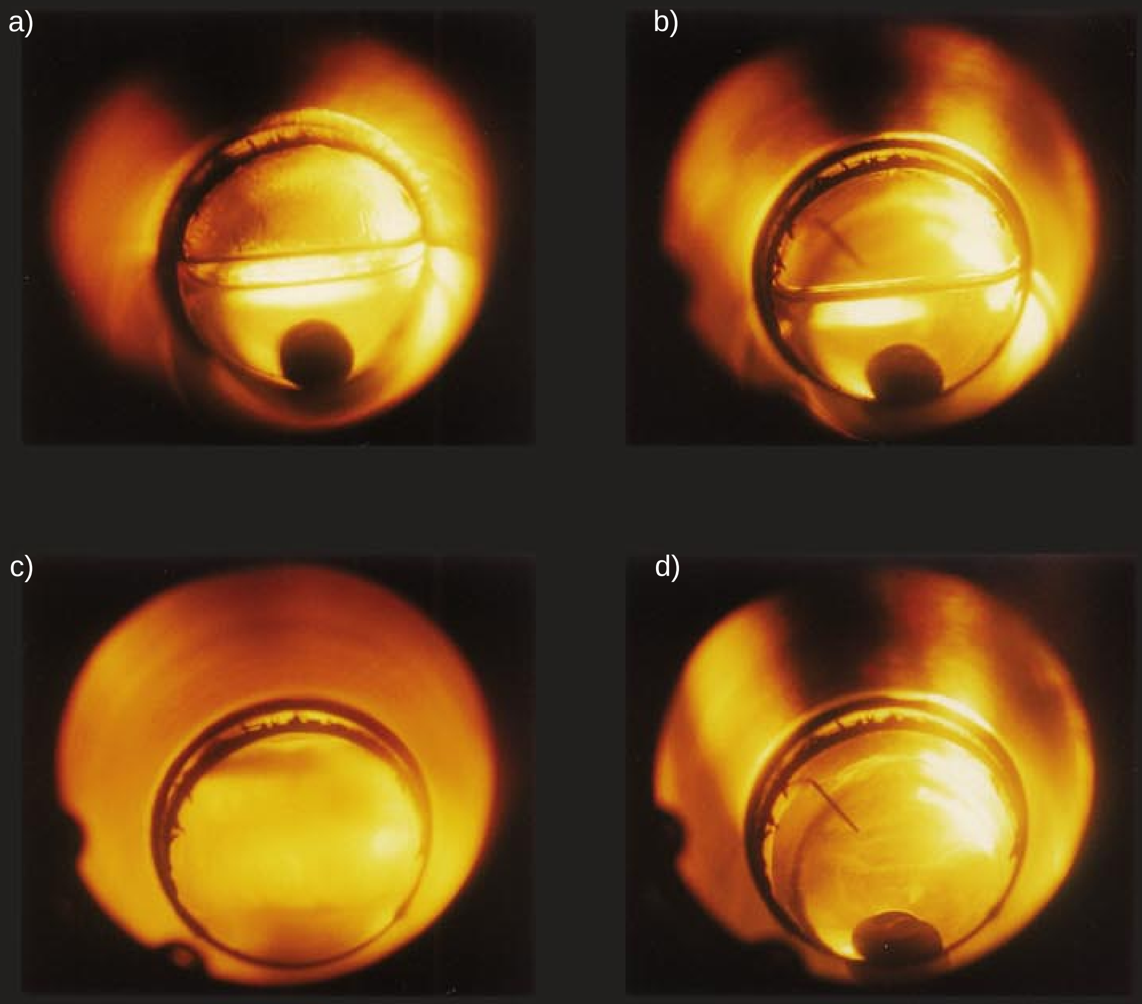
The disappearance of phase boundaries in the water/cyclohexane system (80/20 wt %): a) 25 °C, b) 250 °C, c) at the critical point, d) above the critical point. See also explanations in the review.



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Chemistry in Supercritical Water

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Dedicated to Professor Hans-Jürgen Quadbeck-Seeger on the occasion of his 60th birthday

Growing research activity in the field of supercritical fluids as a reaction medium has been observed since the end of the 1980s. In more recent times attention has been increasingly devoted to supercritical water. As a ubiquitous reaction medium it not only affords advantages from the points of view of ecology, economics, and safety, but it is also of particular interest on account of its solvent parameters (ionic product and dielectric constant), which can be adjusted over a range by means of pressure and temperature. For improving production, purely physical parameters (pressure and temperature) can be altered without the need for a change in solvent, which would be tantamount to a redesign of the entire plant. However, high temperatures and high pressures—the critical parameters for water being 374.2 °C and 22.1 MPa—entail high specific investments. Furthermore, upon use of conventional reactor materials high levels of corrosion occur, so that the search for corrosion-resistant reactor materials and also catalysts is an important research task. Moreover, in the supercritical range of pressures and temperatures there is a shortfall of thermodynamic data for aqueous multicomponent systems, which are indispensable for the correct kinetic description of a reaction. To explore the potential of supercritical water for synthesis, it is therefore essential to devote equal attention to corrosion, thermodynamics, and chemical kinetics. Classes of reactions for which supercritical water is particularly suitable as reaction medium are hydrolyses, hydrations, dehydrations, and oxidations. The potential of supercritical water for syntheses involving these classes of reactions was investigated by means of pilot experiments on model substances. The reactions considered in some detail are the hydrolysis of ethyl acetate, reactions of acetonitrile and acetamide as well as the dehydration of 1,4-butanediol. Studies of the kinetics of the reactions were supplemented by measurements of corrosion and determinations of density and phase boundary lines in subcritical and supercritical aqueous solutions.

Keywords: corrosion · hydrolyses · kinetics · oxidations · supercritical fluids

1. Introduction

The trend towards using supercritical fluids in chemical practice intensified only at the beginning of the 1980s. Technical processes with carbon dioxide as supercritical medium were developed (decaffeination and hop extraction); initial approaches for this purpose were already in existence in the 1950s.[1] Furthermore, owing primarily to the special solvent properties of supercritical fluids, supercritical fluid chromatography (SFC) and the dissolution and subsequent precipitation of particles having adjustable particle size distributions (RESS, SAS)[2] now form part of industrial practice.[1, 3]

Supercritical water (SCW[**]) has been growing in importance as a medium for chemical reactions for about ten years.[4] This is attributable primarily to relatively recent targets set in waste water treatment, namely, the elimination of poorly biodegradable substances. It is possible to convert these substances into less toxic and more readily degradable compounds.[5] In that time there has been a marked rise in general interest in the use of the special *pVT*-dependent

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[**] The abbreviation SCW designates in particular water in the supercritical state, that is, $T > T_c$ (374.2 °C) and $p > p_c$ (22.1 MPa). The term has been extended in this review to cover the subcritical region, that is, $250\,^\circ C \leq T \leq 450\,^\circ C$ and $p > p_c$.

physical properties of SCW. Further, it is only very recently that the potential for synthesis which SCW chemistry affords has caught the eye of chemists.

Many technically important syntheses are afflicted by the selectivity–conversion problem; that is, starting from the reactants and products there are also reaction pathways which lead to unwanted byproducts (reaction networks). Reactions proceeding with nearly 100% yield are rare. Important items in the chemist's toolkit for optimizing these reaction networks with respect to the desired product are usually catalysts, in addition to the classical process parameters of temperature, pressure, and concentration. An additional fine-tuning knob which every synthetic chemist loves to twiddle is the choice of reaction medium, that is, the solvent. However, for the industrial chemist a change in solvent in process development is associated with very high expense, since the entire work-up procedure must be altered.

A key advantage of chemistry in SCW is the possibility of varying the properties of the reaction medium over a wide range solely by changing the pressure and temperature and

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thus optimizing the reaction without changing solvent. This can be seen particularly clearly in the variation of the relative static dielectric constant ε and the pK_w value as a function of temperature and pressure (see Table 1), two physical properties which have a decisive effect on polarity and acid/base-catalytic properties. Furthermore, the reaction kinetics can be strongly affected in the supercritical region by varying the pressure (kinetic pressure effect). In addition, many nonpolar organic substances (e.g. cyclohexane) and gases (e.g. oxygen) are highly soluble in SCW so that restrictions in mass transfer due to phase boundaries do not apply.

The possibilities described are based in the final analysis on the ability of water to can give rise to unique spatial structures through hydrogen bonding. Changes in these structures result in significant modifications in physicochemical properties.[6–8]

In summary, SCW has great potential with regard to the optimization of chemical syntheses. There are, however, drawbacks arising from working at high pressures (high investment costs), the problem of corrosion (expensive materials), and the lack of kinetic and thermodynamic data. For these reasons applied research in the field of chemistry in SCW must not remain confined to synthetic chemistry, but rather also address the issues concerning materials and thermodynamics.

2. Water in the Supercritical State

Important physicochemical properties of water are presented in Table 1 as a function of pressure and temperature.[9, 10] The density ρ of SCW can be changed continuously from high (liquidlike) to low (gaslike) values without phase transition by varying the pressure and temperature.

The high relative static dielectric constant ε of 78.5 at 25 °C drops to a value of about 6 at the critical point, thus clarifying the difference in the solution properties of SCW by comparison with normal water. The reasons for the relatively low value of the dielectric constant are found in the reduced number of hydrogen bonds[11, 12] brought about by the density and temperature. At high pressure (i.e. high density) substances with ionic bonds (e.g. KCl, Na_2SO_4, NaOH) can be dissolved, and at low density nonpolar organic substances (e.g. cyclohexane) and gases (e.g. oxygen) can be dissolved. In the latter case SCW behaves almost like a nonaqueous solvent. According to quantum-mechanical calculations the molecules of supercritical water take part in the breakage and formation of chemical bonds by significantly lowering the activation energy.[13]

In the supercritical region supercritical water exhibits very high specific heat capacities c_p (e.g. 29.2 $kJ\,kg^{-1}\,K^{-1}$ at 400 °C and 29 MPa),[10] so that c_p can vary continuously over a wide range depending on the pressure and temperature. In highly exothermic reactions, such as partial oxidations in SCW, this could diminish the problem of hot spots.

The ionic product of water K_w is heavily dependent on density and temperature, so that this property can be used for optimizing acid/base-catalyzed reactions. At $pK_w \leq 14$ water is more suitable as a medium for heterolytic reactions, and at $pK_w \geq 14$ it is more suitable for homolytic reactions.[14] However, the transition from heterolytic to homolytic is fluid and not sharply demarcated.

The dynamic viscosity η decreases with temperature at high density (collisional transfer of momentum) and increases with temperature at low density (translational transfer of momentum). At moderate supercritical temperatures and high densities η is only a tenth to a twentieth of its value under normal conditions.[13] This leads to the expectation of advantages with regard to selectivity and space-time yield, especially in the case of heterogeneously catalyzed reactions, in which the overall reaction rate is often limited by mass transfer to and from the active centers.

The attribution of a physical effect as the cause for the course of a particular chemical reaction in SCW is complicated since all the physical properties are highly dependent on temperature and pressure. Moreover, water can appear as a reactive component as well as a catalyst.[15–17] Thermodynamic data for pure water are available over a wide range of pressures and temperatures.[10, 18] However, apart from a few binary systems which have been investigated corresponding data for aqueous multicomponent systems are often lacking (see Section 4). In these cases the lack of data on pressure- and temperature-dependent specific volumes especially needs to be emphasized. These allow the exact determination of residence times in continuously operated reactors. Such data can be determined only by means of many experiments.

3. Reaction Kinetics in Supercritical Fluids

On account of the high compressibility of supercritical fluids special importance is attached to pressure when carrying out chemical reactions in these media. Apart from the process parameters of temperature and concentration the rate constant k_x of a reaction can be greatly affected by the pressure. The relationship given in Equation (1) applies,[19, 20]

Table 1. Physicochemical properties of water as a function of temperature and pressure.[9, 10]

	"Normal" water	Subcritical water	Supercritical water		Superheated steam
T [°C]	25	250	400	400	400
p [MPa]	0.1	5	25	50	0.1
ρ [$g\,cm^{-3}$]	0.997	0.80	0.17	0.58	0.0003
ε	78.5	27.1	5.9	10.5	1
pK_W	14.0	11.2	19.4	11.9	–
c_p [$kJ\,kg^{-1}\,K^{-1}$]	4.22	4.86	13	6.8	2.1
η [mPa s]	0.89	0.11	0.03	0.07	0.02
λ [$mW\,m^{-1}\,K^{-1}$]	608	620	160	438	55

$$\left(\frac{\partial \ln k_x}{\partial p}\right)_{T,x_i} = \frac{-\Delta V^{\ddagger}}{RT} \quad (1)$$

where $\Delta V^{\ddagger}$ is the molar volume of activation, which is often interpreted as the change in molar volume in going from the reactants to the transition state. However, this physicochemical interpretation of the volume of activation has to be treated with caution, especially in more complex reactions; in such cases $\Delta V^{\ddagger}$ should be considered as only a purely formal fitting parameter for the quantitative description of the dependence on pressure. Since in the case of supercritical reactions the absolute value of the volume of activation $\Delta V^{\ddagger}$ is often high, substantial variations in rate constants can be achieved here.

The volume of activation is usually split into two terms [Eq. (2)].[13] The first term is an expression of the difference in molecular size between the reactants and the transition state

$$\Delta V^{\ddagger} = \Delta V_1^{\ddagger} + \Delta V_2^{\ddagger} \quad (2)$$

(intrinsic or reaction-specific term). The second term provides information about the interactions between reactants and solvent molecules (extrinsic or solvent-specific term). In supercritical fluids the latter usually predominates and hence determines the pressure dependence of the kinetics. Reactions in supercritical fluids are decisively influenced by these solvent-specific interactions and their unusual solution properties.

As in normal fluids the physical properties in the neighborhood of a dissolved particle are also fundamentally different from the average value for the solution; this is described as a "clustering" or "cage" effect. This cluster formation, which occurs more intensely in supercritical fluids, means that there is a local increase in density, and the molecules involved in the cluster are in dynamic equilibrium with the solvent molecules. A local diminution in density around dissolved particles is also possible.[21] This behavior can become apparent in different ways in terms of reaction kinetics, and each case has to be considered separately on the basis of the theory of collisions in solution.[22] In reactions controlled by diffusion, the rate of reaction can be increased in the fluid phase by a reduction in viscosity and the increased diffusion of the reactants associated with this. On the other hand, however, barriers to diffusion can also be erected by the cage effect.[23]

The rate of a reaction is also controlled by the probability of decomposition of the activated complex (energy transfer from the activated complex to the reaction medium). Supercritical fluids are characterized by particles possessing high mobility (high reaction rate) and simultaneously high density so that this energy transfer is favored.[24] Furthermore, the model of unimolecular reactions postulated by Lindemann applies, making it possible to draw up a detailed reaction mechanism in accordance with the RRKM theory with incorporation of partition functions on the basis of statistical mechanics.[22] For example, a detailed reaction mechanism with a total of 184 elementary reactions is given for the oxidation of methanol and hydrogen in SCW.[25]

Of interest with regard to exercising influence on chemical reactions in SCW is the mode of action of a cosolvent. With a cosolvent the solubility of a substance can be increased considerably, especially when strong hydrogen-bonding or Lewis acid–base interactions occur between the solvent molecules. The solubility of the solute can be augmented by a factor of 10 to 100 owing to the increase in molecular interactions between the solvent and dissolved particles.[21]

4. Mixed-Phase Thermodynamics of Supercritical Fluids

The phase diagram of a pure substance is simple and easy to comprehend. The substance is in the supercritical state when its temperature and pressure are higher than their critical values (Figure 1a). In the case of binary mixtures the phase diagram is extended by one degree of freedom, the concentration. A simple binary mixture (continuous critical curve) at constant temperature with one supercritical component is supercritical at all pressures higher than the critical pressure of the mixture. Accordingly, the critical pressure here is the upper boundary of the two-phase region (Figure 1b).[26]

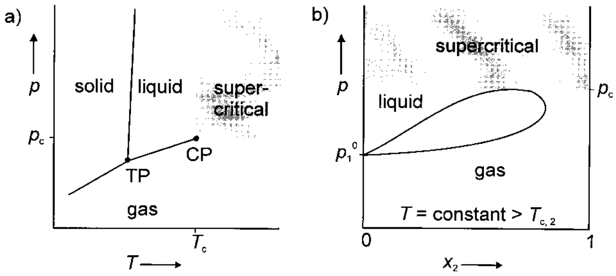


Figure 1. Phase diagrams (schematic).[26] a) Supercritical region of a pure substance. TP: triple point, CP: critical point, p_c: critical pressure, T_c: critical temperature. b) Supercritical region of a simple binary mixture with a supercritical component 2. p_1^0: vapor pressure of component 1, x_2: mole fraction of component 2, $T_{c,2}$: critical temperature of component 2.

The phase diagrams can be classified into six main types in accordance with Van Konynenburg and Scott.[27] For mixtures with yet more components—as is the case for even the simplest of chemical reactions—the phase diagrams are so complex that they cannot be determined with finite effort. Attempts have already been made to carry out calculations for such complex mixtures with the aid of equations of state.[28, 29] There is, however, an added difficulty in that these are reacting systems whose composition changes over time. The mixed-phase thermodynamic description of these reacting supercritical systems is an unsolved problem. This may be one reason among many others for the technical application of supercritical fluids having mainly been limited in the past to thermal separation processes (e.g. fluid/solid and fluid/liquid extraction processes). In these processes no chemical changes take place. The phase diagrams are thus accessible by experiment and hence capable of mathematical description, which makes reliable scale-up from the laboratory to the industrial scale possible.

Since SCW has so far played a secondary role as a solvent and reaction medium, there are only a few systematic studies of the phase behavior and the densities of mixtures with organic substances.[30, 31] These data, however, are indispensable for studying reaction kinetics and designing industrial plants. The determination of phase boundary lines is presented below for the water/cyclohexane system by way of example. Cyclohexane is a potential reactant for partial oxidations (oxidation of cyclohexane to cyclohexanol/cyclohexanone) as well as a possible cosolvent with water (see Section 3).

There are no generally applicable mathematical models for calculating the densities of complex mixtures in the subcritical and supercritical regions. Although various general equations describing the density of liquids under high pressures[32, 33] became established as early as the beginning of the 20th century, their validity is mainly limited to pure substances and to low temperatures. The differences in density relative to pure water which occur may be explained with the example of the water/methanol system.

4.1. Experimental Section

All measurements were carried out in a 30-mL cylindrical optical cell made of Inconel 625 (Figure 2). Two oppositely placed, graphite-sealed sapphire windows allow the visual observation of the whole of the interior.[34] To ensure thorough mixing a magnetic rod made of an aluminum-nickel-cobalt alloy, and encased in Inconel 625 to protect it against corrosion, is used. A permanent magnet rotating outside the cell causes the magnetic rod to rotate. The temperature of the viewing cell is controlled by means of cartridge heaters distributed over the circumference. The temperature is measured by means of a thermocouple in the interior. Two screw presses serve to convey the components into the previously evacuated viewing cell and to generate pressure afterwards.

Figure 2. Optical cell with seals and sapphire windows for the measurement of phase boundary lines and densities in SCW. See text for details.

4.2. Phase Boundary Lines for the Water/Cyclohexane System

In the determination of the phase boundary lines the industrially relevant range of 200 to 400 °C and 20 to 36 MPa was investigated.[35, 36] Phase boundary lines for the two-phase (liquid/gaseous) and the single-phase (fluid) states were recorded. Defined quantities of the two components were metered into the cold viewing cell using the screw presses. The pressure is brought up to the saturated vapor pressure by subsequent heating. The phase transition is identified visually. By varying the pressure and determining the corresponding temperature it was possible to obtain several phase transitions for a mixture and thus establish the course of the phase boundary line. Such isopleths were determined for mixtures of different composition so that it was possible to establish the phase boundary surface and the course of the critical curve in the region studied. The results of these measurements are presented in Figure 3.

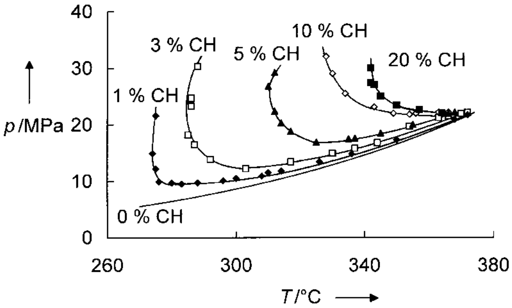


Figure 3. Isopleths of the water/cyclohexane (CH) system.

The phase boundary curves of the mixtures exhibit a minimum and rise steeply as the pressure is increased. This indicates a type 3 phase diagram according to the classification of Van Konynenburg and Scott.[27] This is in agreement with the results of Schneider et al., who studied the water/cyclohexane system at higher concentrations of cyclohexane.[36] Studies on the water/*n*-hexane system also revealed similar behavior.[31] As the concentration of the organic component decreases the single-phase region is shifted to lower temperatures and pressures.

The frontispiece (p. 2998) shows the disappearance of the phase boundaries with rising pressure and temperature. At 25 °C and corresponding vapor pressure three phases are discernible: water phase, cyclohexane phase, and gas phase (a). Above 250 °C the two liquid phases merge (b). At the critical point some clouding and in some cases complete blackout occurs (c). In the supercritical region only a homogeneous fluid phase remains (d).

4.3. Determination of the Densities of Water/Methanol Mixtures

To be able to determine the reaction kinetics for the partial oxidation of methane (see Section 6.5.2) in supercritical water the density of the reaction mixture is needed. To obtain the density defined quantities of a mixture of water and methanol are metered by means of the screw presses into the heated viewing cell. Since the volume of the viewing cell is known the density of the mixture can be calculated. By adding further material in this way at constant temperature different pressures can be established and the associated densities determined. By way of example in Figure 4 the densities of a mixture containing 5 wt% of methanol as a function of pressure and temperature are compared with that of pure water. The difference in density between the mixture and pure water becomes smaller as the temperature rises.

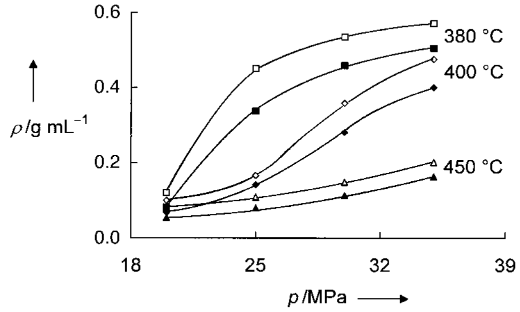


Figure 4. Density of a water/methanol mixture with 5 wt% methanol (filled symbols) and of pure water (open symbols) at three different temperatures as a function of pressure.

5. Corrosion of Metallic Materials in Supercritical Aqueous Solutions

There is so far no universally applicable material which can withstand the reaction conditions in aqueous supercritical fluids. In the presence of acids, oxygen, and halogen and sulfur compounds supercritical water has a corrosive action on reactor materials and fittings. Accordingly, the materials must simultaneously be resistant to temperature and pressure up to approximately 500 °C and 50 MPa and also be resistant to corrosion by the substances employed.

Extensive investigations have shown that none of the metallic materials commercially available at present fulfills all these requirements at the same time.[37–42] For example the material Ducrolloy manufactured by powder metallurgy exhibits outstanding resistance to corrosion in supercritical solutions,[43] but it is not suitable as a reactor material on account of its low tensile strength and expansion characteristics. The problem can be solved in part through structural measures by carrying out the reaction in a corrosion-resistant inner tube which is fitted in a pressure-bearing container. The requirements for reactor fittings and packings such as heterogeneous catalysts, support materials, and linings then reduces to resistance to temperature and corrosion. Another approach to a solution consists of coating the materials.

The specific rate of change in mass of nickel alloys in SCW is particularly high at high pressures, in correlation with the ionic product of water.[38–42] In the presence of phosphoric acid, however, marked pitting occurs even at low pressures. It is postulated that the cause of this is the formation of low-melting nickel(III) phosphates.[42] Kriksunov and MacDonald[44] developed a model in which the specific rate of change in mass can be calculated as a function of density, H^+ concentration, and oxygen concentration. In summary, there is still a high need for research in this field since the underlying corrosion mechanisms are still not adequately understood.

5.1. Experimental Section

In this section by way of example the behavior of copper and silver as potential oxidation catalysts together with iridium as reactor coating material under the influence of supercritical aqueous solutions will be described as a function of temperature, pressure, and chemical composition. The corrosive media employed were pure water, aqueous acetic acid (as a model substance for the carboxylic acids produced in partial oxidations), and aqueous solutions containing oxygen (hydrogen peroxide served as the source of oxygen).

The experiments were carried out in continuous high-pressure equipment the central component of which is a 250-mL autoclave made of the nickel-based alloy Inconel 625 (wall thickness 25 mm, metallic sealing). Inconel 625 has proved to be effective in SCW both under acid as well as oxygenated conditions and has exhibited adequate stability. The aqueous solutions were conveyed through an electric preheater made of Inconel 625 and through the autoclave with the aid of a high-pressure diaphragm pump. The material leaving the reactor was cooled and decompressed in two stages.

The corrosion studies were carried out at temperatures of 330 to 410 °C and pressures of 25 to 35 MPa since the physical properties of the aqueous media employed vary particularly markedly in this range. Before and after treatment the samples were characterized by gravimetry, optical microscopy, scanning electron microscopy, energy-dispersive X-ray analysis, and X-ray diffraction. The metal ion concentrations in the aqueous solutions from the reactor were analyzed with the aid of atomic absorption spectroscopy.

The test materials were available in the form of metal plates (10 × 10 × 1 mm) and powders. Compacts (diameter 9 mm, thickness 1 mm) were prepared from the metal powders using a hydraulic press, and these were sintered at suitable temperatures in an atmosphere of nitrogen. By appropriate choice of the compacting pressure and sintering conditions (temperature, heating rate, heating time) surfaces of the order of $1\,m^2g^{-1}$ (in accordance with Brunauer, Emmett and Teller) were produced.

5.2. Corrosion Behavior in Water

The materials investigated were resistant in pure SCW; changes in mass for copper, silver, and iridium were below the limit of detection. Surface changes were not discernible under the scanning electron microscope.

5.3. Corrosion Behavior in Water/Acetic Acid

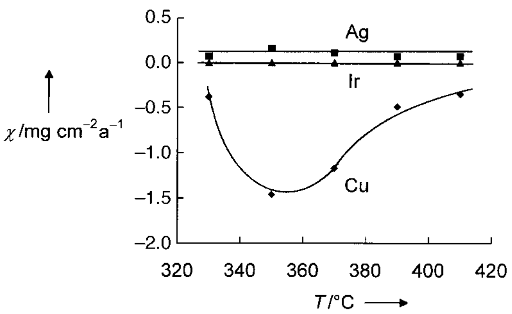


Figure 5. Specific rate of change in mass χ ($a=$ year) for silver, iridium, and copper in an aqueous solution of acetic acid (3 wt %) as a function of temperature at 25 MPa.

The results of the action of aqueous acetic acid on the test materials at 25 MPa are presented by way of example in Figure 5. The specific rate of change in mass χ for copper is greatest just below the supercritical region. This may be explained by the relatively high dissociation constants of water and acetic acid in this subcritical region (Table 1). When the temperature is increased further and the supercritical region attained χ falls distinctly once more. However, even in the least favorable case of $\chi = -1.46$ mg cm^{-2}a^{-1} the values for copper are still very low. By varying the pH value through the addition of acetic acid the effect of acid concentration on the corrosive attack of copper was also examined.[45] In the subcritical region χ increases distinctly on addition of acetic acid. Here water and acetic acid are present in more highly dissociated form than in the supercritical region.[44] The increased number of ions favors electrochemical and acid-induced corrosion. Increasing the acid concentration from 1.5 to 6 wt % causes the χ values to be trebled. In the supercritical region increasing the acid concentration has no effect since here the aqueous acetic acid solution is present in a substantially less highly dissociated form.

Silver exhibits no variations in the specific rate of change of mass as a function of temperature. Oxide layers, which could be postulated to explain the slight increase in mass found, are not discernible. Energy-dispersive X-ray analysis and X-ray diffraction studies after the experiments demonstrated only the presence of pure silver. One possible explanation for the increase in mass is the intercalation of oxygen, which was present in the water used at a concentration of 8 mg L^{-1}. It is known that silver can absorb considerable amounts of oxygen in its lattice.[46, 47]

Iridium, the potential reactor coating material, is inert to supercritical acetic acid solutions. No changes in mass or to the surface are observed.

5.4. Corrosion Behavior in Water/Oxygen

Figure 6 illustrates the effects of oxygenated aqueous solutions on the test materials. Adherent oxide layers are formed on the surface of copper (375 °C, 25 MPa). X-ray diffraction analyses demonstrated that these are copper(I) and copper(II) oxide layers.[45] They passivate the metal to further attack. The formation of the oxide layer has already gone to completion after 20 h, and the rate of formation of the oxide layer is largely independent of temperature in the range under study.

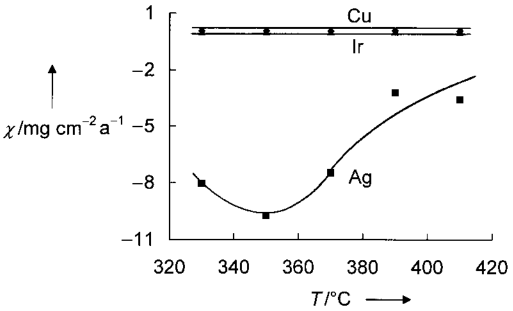


Figure 6. Specific rate of change in mass χ for copper, iridium, and silver in an aqueous solution containing oxygen (1.4 wt %) as a function of temperature at 25 MPa.

In oxygen-containing aqueous solution silver exhibits high specific rates of change in mass, the maximum value being almost $\chi = -10$ mg cm^{-2}a^{-1}. This is attributed to the instability of silver oxides under these conditions.[48] The effect is most pronounced in the subcritical region, due once more to the high ionic product. Long-term tests showed that this is a uniform general attack.

The potential reactor coating material, iridium, is stable in oxygenated solutions (no changes in mass or to the surface). More extensive tests with chlorine-containing additives at 300 to 400 °C and 25 MPa demonstrated that iridium is a very stable material even under these conditions. However, its poor workability caused by its high melting point of 2410 °C is a problem.

6. Potential for Syntheses

Water in its supercritical state is a very reactive substance, permitting chemical reactions without the addition of strong acids or bases. Such reactions can be used for synthesis, recycling of waste, and refining of biomass. Some examples are shown below.

Studies by Korzenski and Kolis[49] show that Diels–Alder reactions can be carried out in SCW. For example, in the reaction of 2,3-dimethyl-1,3-butadiene with acrylonitrile at 293 °C and with a residence time of 25 min, 3,4-dimethylcyclohex-3-enyl cyanide was obtained in 100 % yield. In comparative reactions of different dienes with electron-deficient dienophiles in SCW it was possible to demonstrate higher yields and purer products than under conventional conditions. The occurrence of polymerization products in anhydrous reactions was markedly suppressed.

Organometallic reactions have so far been carried out mainly in supercritical carbon dioxide and will not be considered further here. Very few reactions in SCW are described, but among them is the successful cyclotrimerization of acetylene under CpCo catalysis.[50]

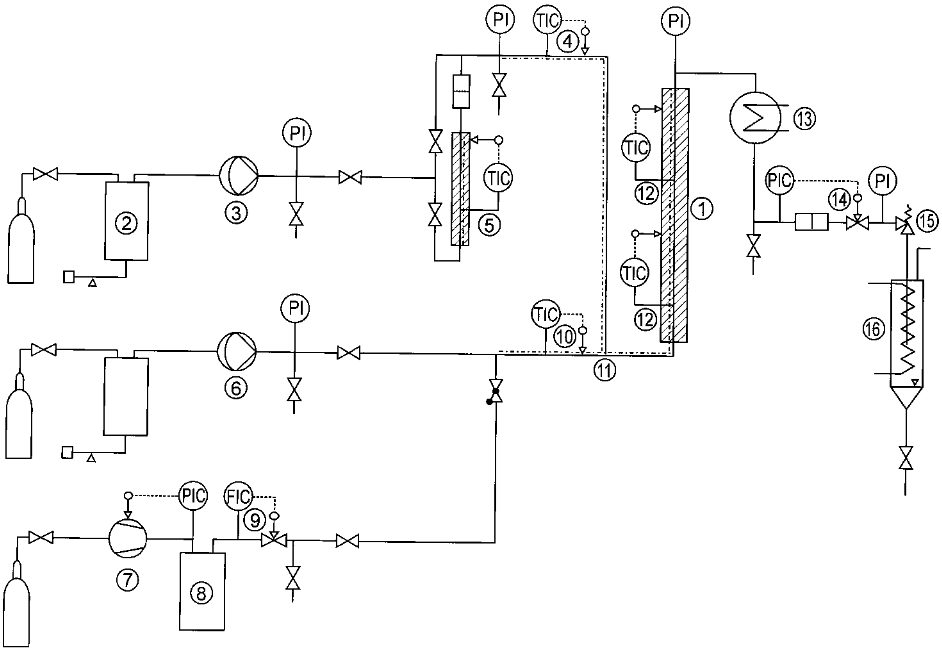


Figure 7. Flow diagram of the high-pressure installation for reactions in SCW. See text for explanations. FIC = flow indication and control, PI = pressure indication, PIC = pressure indication and control, TIC = temperature indication and control.

Organic geochemical processes proceeding under hydrothermal conditions such as the formation of petroleum are of great interest. To arrive at a better understanding of these processes various groups have been studying reactions of model constituents under hydrothermal conditions. Klein et al.[51, 52] employed the compounds $PhCH_2XPh$ (X = CH_2O, O, NH, S) and $PhCH_2XYPh$ (XY = CH_2CH_2, OCH_2, CH_2O).

Apart from the total oxidation of organic compounds (SCWOs) partial oxidation reactions in SCW have also been studied. In the oxidation of methane at 380 °C and a pressure of 30 to 60 MPa 15 to 20 % of the carbon consumed appeared in the form of methanol.[53]

A further interesting field of application of supercritical water is the degradation of biomass, the fluidization of wood, and the degradation of lignocellulose material. Since the biomass contains 40–50 wt% of cellulose, D-glucose is suitable as a model substance. Following its degradation in SCW it was possible to detect inter alia 5-hydroxymethylfurfural in relatively large concentrations.[54] Antal et al.[55] carried out acid-catalyzed dehydration reactions on various low molecular weight alcohols, such as ethanol and propanol, in order to obtain more detailed information about the OH functionality in the cellulose polymer and its reactivity under subcritical and supercritical conditions. Useful surveys may be found from Savage et al.[23] and Subramaniam and McHugh.[56]

6.1. Experimental Section

To explore the synthetic potential of SCW, hydrolysis, hydration, dehydration, and partial oxidation reactions as well as other reactions of various model substances were carried out in the subcritical and supercritical regions without the addition of mineral acids and bases. An attempt was thus made to overcome the disadvantages of classical reaction methods (inter alia catalyst and neutralization costs, production of salt and low space–time yields). Most investigations in SCW have so far taken place either in batch vessels or small reactors, so that wall effects arising from the corresponding reactor material could not always be excluded. For this reason a continuous system was constructed with which throughputs of 4 L h^{-1} are possible. The maximum operating conditions were chosen to be 50 MPa and 500 °C, which may be regarded as realistic upper limiting values for industrial applications. The centerpiece of this system (Figure 7) is a tubular reactor ① made of Inconel 625 (having an internal volume of 10 or 50 mL depending on the thickness of tube used), with which residence times of between 5 and 400 s may be achieved.

From a supply vessel ② under nitrogen pressure water is metered in through a weigh-controlled diaphragm pump ③ and brought up to reaction temperature my means of a resistance heater ④. A reactor ⑤ capable of being heated can optionally be connected in series ahead of this in order to introduce molecular oxygen into the reactor from the silver-catalyzed decomposition of hydrogen peroxide. The organic component is conveyed in the same manner through a second diaphragm pump ⑥. Organic gases such as methane are first transported by a diaphragm compressor ⑦ into a pressurized storage tank ⑧, from which a stream is withdrawn at a steady rate with a mass flowmeter ⑨ and fed to the reactor through an electric preheater ⑩.

The streams are combined in a mixing head ⑪ and conducted into the reactor. The nickel-based alloy used, Inconel 625, has proved to be effective in corrosion tests (see Section 5) carried out in SCW and exhibited adequate stability. The tubular reactor used is maintained at the required operating temperature with the aid of an electrically heated two-zone tubular furnace ⑫. The hot discharge from the reaction traverses a cooling section ⑬ and a filtering unit, and after this it is decompressed to ambient pressure through a control valve ⑭ constructed in two stages and an overflow valve ⑮ in order to avoid cavitation damage to the valve seats.

The material discharged from the reactor is separated into a liquid and a gas phase in a cooled phase separator ⑯. The liquid components are analyzed by GC-MS (qualitative) as well as by GC-FID and HPLC (quantitative). In the case of the hydrolysis of poly(tetrahydrofuran diacetate) and poly(tetrahydrofuran) (see Sections 6.2.3 and 6.2.4) the products discharged from the reactor were analyzed by means of SFC/

CI-MS. Gaseous components were quantified by GC-TCD (TCD = thermal conductivity detector). The gas chromatographs have an external preevaporation device based on that developed by Deans[57] with a coupled gas metering system. If not stated otherwise the experiments were carried out at 250 to 450 °C and 23 to 35 MPa using a mean residence time of 2 min and a reactor admission concentration of 5 wt % for the organic substance.

6.2. Hydrolyses

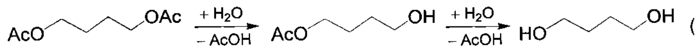
6.2.1. Simple Carboxylic Acid Esters

The hydrolysis of ethyl acetate proceeds selectively to form acetic acid and ethanol [Eq. (3), R = Et]. Only above 350 °C are small quantities of ethylene, CO, and CO_2 found in the gas phase. At a reaction temperature of 350 °C and with residence times of 150 s or more almost complete conversion was achieved (see Section 7.1). To investigate the effect of the ester group the hydrolysis of methyl, *n*-butyl, and benzyl acetate was carried out. The rate of hydrolysis rises in the sequence benzyl > methyl > ethyl > *n*-butyl. The equilibrium conversion ratios achieved are 88 % for methyl acetate, 98 % for ethyl acetate, 60 % for *n*-butyl acetate, and 44 % for benzyl acetate.

$$CH_3COOR \xrightarrow{+H_2O} CH_3COOH + ROH \qquad (3)$$

6.2.2. 1,4-Butanediol Diacetate

1,4-Butanediol diacetate served as a model substance for the hydrolysis of poly(tetrahydrofuran diacetate), an intermediate in the synthesis of poly(tetrahydrofuran). The reaction proceeds in a manner comparable to the hydrolysis of ethyl acetate [Eq. (4)]. In the subcritical region the conversion rises from 39 % at 250 °C to nearly 100 % at 350 °C. On passing through the critical point it first falls slightly and then rises again to 97 % when the temperature is raised further to 400 °C. In addition to 1,4-butanediol, tetrahydrofuran (THF) is also formed at temperatures above 350 °C.



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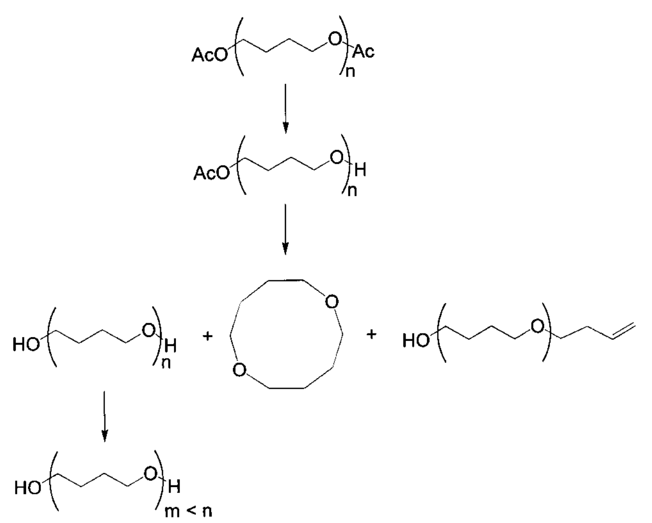
6.2.3. Poly(tetrahydrofuran diacetate)

On account of the saponification of 1,4-butanediol diacetate described in Section 6.2.2, the hydrolysis of poly(tetrahydrofuran diacetate) was also investigated (Scheme 1). At 250 °C the products have only one acetyl group. At temperatures ranging from 350 to 400 °C poly(tetrahydrofuran diacetate) is completely converted. In addition to poly(tetrahydrofuran), cyclic and olefin species appear.



Scheme 1. Hydrolysis of poly(tetrahydrofuran diacetate) in SCW.

6.2.4. Poly(tetrahydrofuran)

As the temperature is raised poly(tetrahydrofuran) is broken down increasingly rapidly to form small chains having relative molar masses in the range of 200 to 500 (Scheme 1, bottom).

6.2.5. Acetamide and Benzamide

The hydrolysis of acetamide to form acetic acid proceeds almost quantitatively. Acetonitrile is formed only in small quantities (see Section 7.2). The hydrolysis of benzamide proceeds selectively with formation of benzoic acid. In the temperature range of 300 to 400 °C benzamide undergoes hydrolysis more slowly than acetamide, while the reaction is faster than that of acetamide at temperatures above 400 °C.

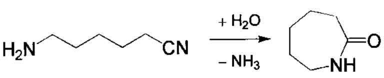
6.3. Hydration Reactions

6.3.1. Acetonitrile and Benzonitrile

On hydration of acetonitrile the only products detected in the liquid phase were acetamide and acetic acid. The ammonia produced is bound in the form of ammonium acetate (see Section 7.2). Benzonitrile reacts to form benzamide and then benzoic acid in accordance with pseudo-first-order kinetics. At 380 °C and 25 MPa the half-life is approximately 8 min. At all the temperatures studied benzonitrile is hydrated to the amide more rapidly than acetonitrile.

6.3.2. ε-Aminocapronitrile

ε-Aminocapronitrile is an intermediate in the production of ε-caprolactam from butadiene. Up to a temperature of 380 °C ε-caprolactam is formed as a stable end product via the intermediate ε-aminocaproamide [Eq. (5), overall selectivity approximately 80 %].



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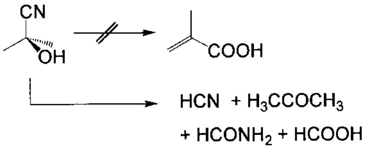
6.3.3. *Acetone Cyanohydrin*

Acetone cyanohydrin is an intermediate in the production of methyl methacrylate by the ACH process. In subcritical and supercritical water decomposition results in the formation of acetone, prussic acid, formamide, and formic acid. Methacrylic acid was not detected (Scheme 2).



Scheme 2. Decomposition of acetone cyanohydrin in SCW.

6.4. Dehydration Reactions

Numerous studies of the dehydration of alcohols in supercritical water have already been carried out. Most of these, however, have involved primary monoalcohols such as ethanol[14, 55, 58] or propanol[59, 60] and more rarely diols such as ethylene glycol[58] or 1,3-butanediol.[61] Olefins were often found as reaction products.

6.4.1. *Ethanol*

Ethanol proved to be kinetically stable in SCW. Dehydration to form ethylene occurs at a significant rate only at elevated temperatures.[55]

6.4.2. *Cyclohexanol*

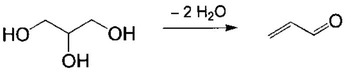
The dehydration of cyclohexanol was investigated under batch conditions at 395 °C and 30 MPa using an initial concentration of 10 wt % and a residence time of 3 h. A batch autoclave made of Inconel 625 having a volume of 1 L was employed for this purpose. Water was put into the reaction vessel first, and the organic substance was added through a screw press after the heating phase until a mass fraction of 10 wt % was attained. In doing so the pressure assumes a level in keeping with the temperature and the quantity of added substance. After the reaction the product is almost exclusively cyclohexene. Thus, despite the excess water the equilibrium lies on the side of the alkene.

6.4.3. *1,4-Butanediol*

In the subcritical and supercritical region 1,4-butanediol is selectively dehydrated to form THF. THF is stable under the chosen reaction conditions. No further decomposition products were found (see Section 7.3).

6.4.4. *Glycerin*

The dehydration of glycerin, a potentially renewable raw material, to form acrolein [Eq. (6)] does not set in to any notable extent until the temperature reaches 350 °C.



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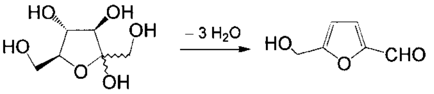
6.4.5. *Fructose*

The industrial production of 5-hydroxymethylfurfural (5-HMF) is particularly interesting since it can readily be converted into furandicarboxylic acid, which is a polymer component similar to terephthalic acid.[54] A simple pathway to 5-HMF is a prerequisite for the production of new polymers based on renewable raw materials. D-Fructose was successfully dehydrated to 5-HMF [Eq. (7)] in the temperature range of 250 to 350 °C and 250 bar with a selectivity of approximately 30 % and with a conversion ratio of approximately 60 %.



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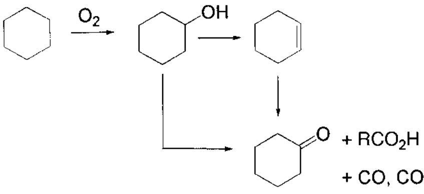
6.5. Partial Oxidation Reactions

6.5.1. *Cyclohexane*

The oxidation of cyclohexane was investigated at a molar ratio of cyclohexane to oxygen of two to one. In pure SCW cyclohexane is stable over the specified ranges of residence times and temperatures. The products identified on addition of oxygen were cyclohexene, cyclohexanol, cyclohexanone, and carboxylic acids together with carbon monoxide and carbon dioxide (Scheme 3). As the temperature goes up from 350 to 400 °C the selectivity in favor of the useful products (-ene, -ol, -one) rises to values of 30 % with complete reaction of the oxygen.



Scheme 3. Partial oxidation of cyclohexane in SCW.

6.5.2. *Methane*

In the studies, the molar ratio of methane to oxygen was ten to one. Methane is stable in SCW up to a temperature of 450 °C.[62] The extent to which the methane reacts rises with increasing temperature and pressure. In agreement with the literature[62–64] the products of methane oxidation found were carbon monoxide, carbon dioxide, methanol, and small quantities of formaldehyde and formic acid [Eq. (8)]. The

$$CH_4 \longrightarrow CH_3OH \longrightarrow CH_2O \longrightarrow HCOOH \longrightarrow CO_2 \qquad (8)$$

highest selectivity achieved in favor of methanol was 39% at 420 °C and 35 MPa with a residence time of 23 s. The associated consumption of oxygen was 13%.

6.6. Other Reactions

6.6.1. Formaldehyde

Formaldehyde is not stable in SCW, and its decomposition is highly dependent on temperature. At temperatures above the critical temperature formaldehyde reacts to completion to form methanol, formic acid, carbon monoxide, and carbon dioxide. Carbon monoxide is the main product at higher reaction temperatures and methanol at lower reaction temperatures (Figure 8). This conversion of formaldehyde by a Cannizzaro reaction into methanol and carbon monoxide (formic acid) affords the possibility of transforming dilute formaldehyde waste water into easily separable methanol (integrated environmental protection).

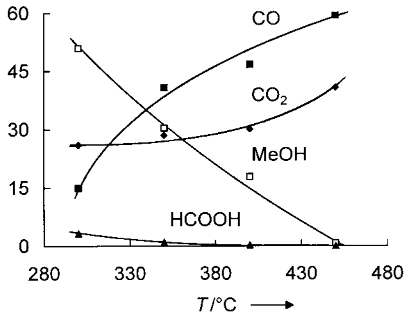


Figure 8. Selectivity S with respect to the products CO, CO_2, methanol, and formic acid in the decomposition of formaldehyde as a function of temperature at 30 MPa and with a residence time of 2 min.

6.6.2. Formic Acid

At low temperatures (300 °C) formic acid decomposes preferentially into carbon monoxide and water. At higher temperatures (>380 °C) the reaction pathway switches to the production of hydrogen and carbon dioxide (Figure 9).[55, 65]

$$CO + H_2O \longleftarrow HCOOH \longrightarrow H_2 + CO_2$$

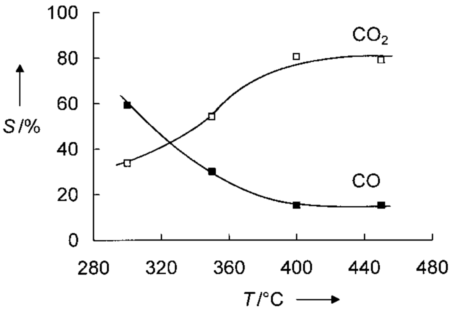


Figure 9. The two decomposition pathways of formic acid and the selectivity S with respect to the products CO and CO_2 as a function of temperature at 30 MPa and with a residence time of 2 min.

6.6.3. Acetic Acid

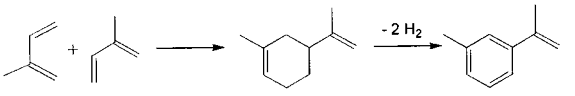
Up to temperatures of 400 °C acetic acid does not decompose. At temperatures above 400 °C limited reaction to the extent of 2% was found. According to Meyer et al.[66] the decomposition of acetic acid in the temperature range of 475 to 600 °C and at 24.6 MPa results principally in methane and carbon dioxide [Eq. (9)]. Accordingly, the decomposition of

$$CH_3COOH \xrightarrow{> 450\,^\circ C} CH_4 + CO_2 \qquad (9)$$

acetic acid does not occur to any significant extent until temperatures above 450 °C are reached.

6.6.4. Isoprene

The reaction of isoprene in SCW was conducted in batch mode (see Section 6.4.2) in the temperature range of 300 to 410 °C at 25 MPa and with an initial concentration of 8 wt%. The residence time was 1 h. The main products were Diels–Alder adducts such as dipentene and some terpenes [Eq. (10)]. No hydration products could be detected.



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7. Kinetic Studies

In Section 6 preliminary studies on the potential of SCW for synthesis were presented. More precise kinetic studies will now be presented with reference to the hydrolysis of ethyl acetate, hydration of acetonitrile, hydrolysis of acetamide, and dehydration of 1,4-butanediol.

7.1. Hydrolysis of Ethyl Acetate

The hydrolysis of ethyl acetate was carried out in the tubular reactor (see Section 6.1) under the following conditions: 23 to 30 MPa, 250 to 450 °C, and a residence time of 5 to 230 s. The concentration–time curves established are shown in Figure 10 for 350 and 380 °C and 25 MPa by way of

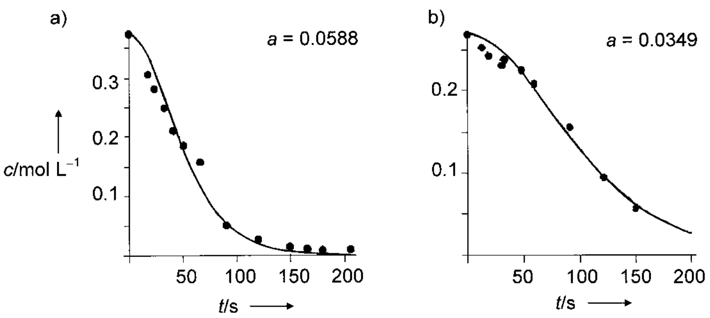


Figure 10. Comparison of the calculated (line) and experimental variation in concentration (dots) in the hydrolysis of ethyl acetate at a) 350 °C, 25 MPa and b) 380 °C, 25 MPa. The parameter a is defined in Equation (13).

example, and they exhibit an S-shaped pattern such as can be expected for an autocatalytic reaction.

The dependence of the conversion on time and temperature, however, was surprising (Figure 11). The highest conversion levels were found at approximately 350 °C; any further rise in temperature led in the supercritical region to a decline in conversion. Both the addition of acetic acid as well as that of sodium sulfate result in accelerated saponification (Figure 12).

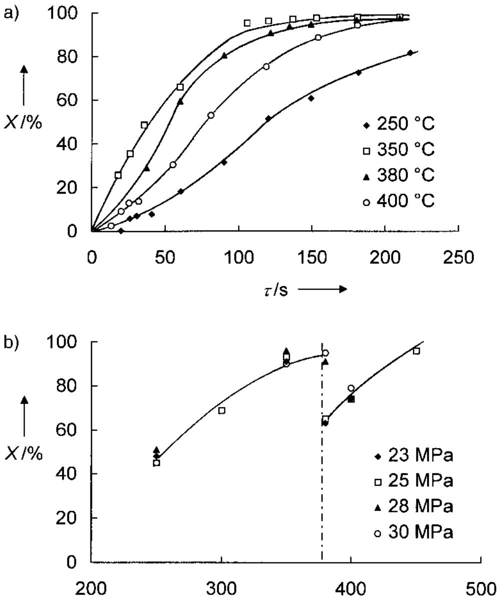


Figure 11. Conversion X in the hydrolysis of ethyl acetate as a function of residence time τ at 28 MPa for four temperatures (a) and as a function of temperature for a mean residence time of 2 min for four pressures (b).

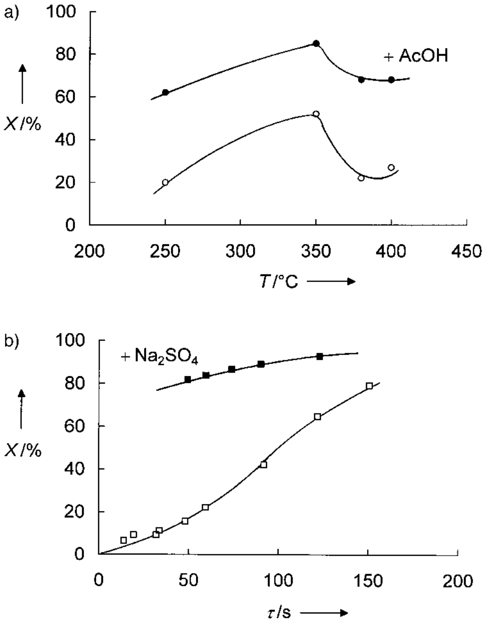


Figure 12. Plot of the conversion X in the hydrolysis of ethyl acetate at 25 MPa a) with a residence time of 60 s with (10 wt %) and without addition of acetic acid as a function of temperature; and b) at 25 MPa and 380 °C with (1 wt %) and without sodium sulfate as a function of residence time.

A number of mechanisms (e.g. $A_{AC}1$, $A_{AC}2$, $A_{Al}1$, $A_{Al}2$) are known for the acid-catalyzed hydrolysis of esters.[67] The $A_{AC}2$ mechanism[68] (Scheme 4, top) occurs most frequently, as has been shown by numerous kinetic studies.[69, 70] This involves specific acid catalysis. Based on the assumptions and boundary conditions presented in the bottom of Scheme 4, the reaction scheme gives rise to the differential equation (11), which is completely soluble with Equation (12); a is defined in Equation (13). The kinetics of the hydrolysis of ethyl acetate

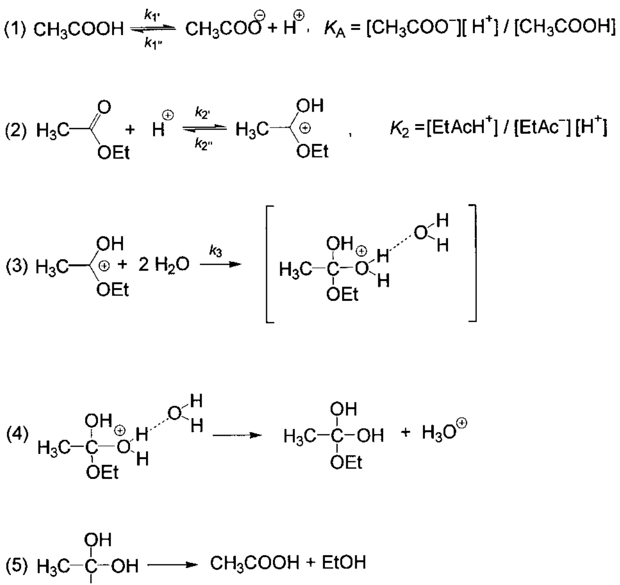
$$\frac{d[EtAc]}{dt} = -k_3K_2[H_2O]^2\sqrt{K_A}[EtAc]\sqrt{[EtAc]_0 - [EtAc]} \quad (11)$$

$$[EtAc] = [EtAc]_0\left[1 - \tanh\left\{\frac{a\sqrt{[EtAc]_0}\,t}{2}\right\}\right]^2 \quad (12)$$

$$a = k_3K_2[H_2O]^2\sqrt{K_A} \quad (13)$$

can be very well described (see Figure 10) by mathematical fitting of the model parameter a to the results of the measurement. In addition to the rate constant k_3 the parameter a also incorporates the equilibrium constant K_2, the K_A value for the acetic acid, and the water concentration.

The water concentration[10] together with the K_A values for acetic acid[71] under the reaction conditions can be obtained from the literature, so that the product of the rate constant k_3 and the equilibrium constant K_2 can be calculated from the parameter a as a function of pressure and temperature. On the assumption that the temperature dependence of k_3 can be



assumptions and boundary conditions:

$[H_2O]$ is a function of T and p

$[AcOH] = [EtAc]_0 - [EtAc]$

$[AcO^-] = [H^+]$

$[H^+] = (K_A[AcOH])^{1/2}$

$[EtAcH^+] = K_2[EtAc][H^+]$

Scheme 4. Top: $A_{AC}2$ mechanism for the hydrolysis of ethyl acetate.[68] Bottom: assumptions and boundary conditions for analyzing the kinetics of this hydrolysis.

approximated by an Arrhenius expression (activation energy E_a) and K_2 by a van't Hoff expression (enthalpy of reaction $\Delta_R H$), the temperature dependence of the product (k_3K_2) is given by Equation (14). Figure 13 shows the form of $\ln(k_3K_2)$

$$\ln(k_3K_2) = -\frac{(\Delta_R H + E_a)}{RT} + \text{const} \qquad (14)$$

as a function of the reciprocal temperature at four different pressures. The curves exhibit a kink above 350 °C at the transition from the subcritical to the supercritical region, which can be interpreted as an indication of a change in the reaction mechanism (see also Figure 11b).[72] The variation of the activation volume[71] can also be evaluated as a further indication of a change in reaction mechanism on passing from the subcritical region ($\Delta V^{\neq} = -100\ \text{cm}^3\text{mol}^{-1}$) to the supercritical region ($\Delta V^{\neq} = +3000\ \text{cm}^3\text{mol}^{-1}$).

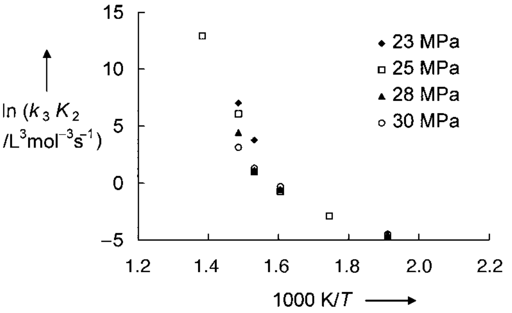
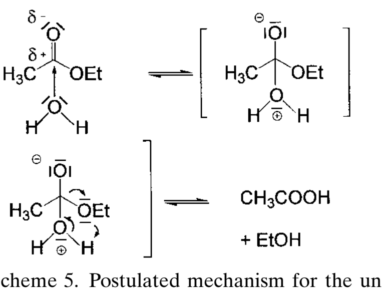


Figure 13. Modified Arrhenius plot of the hydrolysis of ethyl acetate at four pressures.

It is known that apart from an acid-catalyzed mechanism, ester hydrolysis in a neutral medium is also possible (Scheme 5).[73] In the first rate-determining step a water molecule makes a nucleophilic attack on the carbon atom of the carbonyl group of the ester, and then the hydrolysis is concluded by proton transfer with formation of carboxylic acid and alcohol.



Scheme 5. Postulated mechanism for the uncatalyzed hydrolysis of ethyl acetate.[73]

The experimental results described above permit the conclusion that in the subcritical region (250 to 350 °C) ester hydrolysis proceeds preferably by an $A_{AC}2$ mechanism, since here the pK_w value of the water is distinctly lower than 14. In the supercritical region with pK_w values of 19 to 20 a nucleophilic, non-proton-catalyzed mechanism is probably dominant.

7.2. Hydration of Acetonitrile and Hydrolysis of Acetamide

The potential of SCW for syntheses involving the hydration of nitriles was investigated using acetonitrile as model substance (300 to 450 °C and 23 to 32 MPa). The residence time was 10 to 250 s. Reactions of acetamide,[74] isobutyronitrile,[52, 75, 76] benzonitrile,[75, 76] benzamide,[77] and butyronitrile[78] in the subcritical region have already been described.

The reaction of acetonitrile in SCW ensues selectively via the amide to form the carboxylic acid (Scheme 6, Table 2).

$$\text{RCN} + \text{H}_2\text{O} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \text{RCONH}_2$$

$$\text{RCONH}_2 + \text{H}_2\text{O} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \text{RCOO}^- \ \text{NH}_4^+$$

Scheme 6. Mechanism for the hydrolysis of nitriles in SCW. R = Me, Ph.

Table 2. Rate constants k_i [s^{-1}] at 400 °C and 25 MPa as well as activation energies E_a [kJ mol^{-1}] at 25 MPa for the hydrolysis of acetonitrile and benzonitrile in SCW.

	Acetonitrile	Benzonitrile
k_1	4.5×10^{-3}	4.9×10^{-3}
k_{-1}	6.0×10^{-3}	≈ 0
k_2	1.3×10^{-2}	6.8×10^{-3}
k_{-2}	1.0×10^{-8}	≈ 0
E_a	92[a]	109[b]

[a] The value for acetamide is 47 kJ mol^{-1}. [b] The value for benzamide is 111 kJ mol^{-1}.

Under normal conditions the nitrile reacts in a finite time only on addition of strong acids or bases. In contrast, when subcritical or supercritical water is used as solvent and coreactant no additives are needed. As a result, no mineral acids are used, and the subsequent problem of waste water disposal does not arise.

The hydrolysis of acetamide as a successor reaction in the hydration of acetonitrile was investigated separately from the latter under the same reaction conditions. Acetamide does not react exclusively to form the acid, but rather in an equilibrium reaction small quantities of acetonitrile are formed as well as acetic acid.

The measured changes in concentration in the reaction of acetonitrile to form the amide and the carboxylic acid are well described using a pseudo-first-order kinetic model. Figure 14

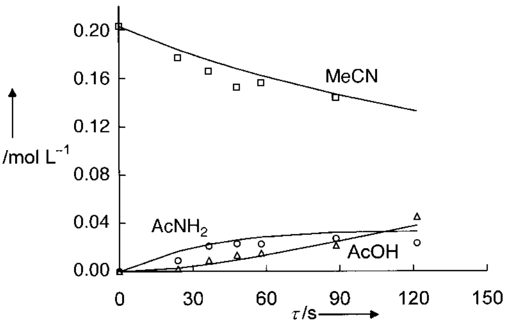


Figure 14. Modeled variation of concentration in the reaction of acetonitrile with water in comparison with values measured at 25 MPa and 400 °C.

shows the simulated changes in concentration in comparison with the measured values. Only when the reaction proceeds beyond 30%, which in these experiments only occurred above 450 °C, is there any significant difference between the model and experiment. Autocatalytic effects due to the acetic acid formed and/or the ammonium acetate formed from it are a possible cause of this. It was possible to obtain support for this assumption by means of experiments in which the products of the reaction were added in advance. Both the addition of acetic acid and ammonium acetate had a marked impact on the extent of reaction. These effects were not taken into account in the kinetic model. The hydrolysis of acetamide proceeds much faster than the hydration of acetonitrile (see Table 2).

Comparison with benzonitrile as a model substance for aromatic nitriles shows that the reaction rates and activation energies are of the same order of magnitude as for acetonitrile (Table 2). By comparison with the hydrolysis of benzamide (model substance for aromatic amides) the hydrolysis of acetamide exhibits lower dependence on temperature, and this is reflected in the activation energies.

7.3. Dehydration of 1,4-Butanediol

The dehydration of 1,4-butanediol to form THF is carried out on an industrial scale today in the liquid phase at elevated temperatures in the presence of a catalyst for the elimination of water, such as sulfuric or phosphoric acid,[79–81] acid salts,[82] or acid ion exchangers. Corrosion and waste disposal problems are the disadvantages associated with this.

The kinetic studies were performed under the following reaction conditions: 5 wt% butanediol in the starting solution, 23 to 35 MPa, 300 to 400 °C, 15 to 165 s residence time. 1,4-Butanediol eliminates water in SCW with a selectivity of almost 100% to form THF, which proved to be stable under the reaction conditions. The measurements may be described by a pseudo-first-order kinetic equation (Figure 15).

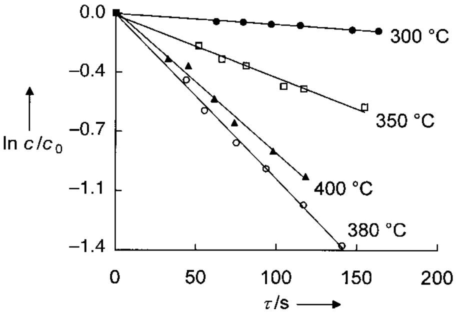


Figure 15. Logarithmic plot of 1,4-butanediol concentrations at a pressure of 30 MPa and four temperatures as a function of residence time τ (initial concentration 5 wt% butanediol).

An increase in temperature in the range of 300 to 380 °C results at all pressures in an increase in conversion, that is, the space – time yield. A further increase in temperature to 400 °C causes the values to fall again. Addition of 1 wt% acetic acid resulted in a marked rise in conversion ratios (Figure 16). The activation energies according to Arrhenius were determined from the temperature dependence of the reaction. They range from 88 to 116 kJ mol^{-1} and tend to rise with pressure.

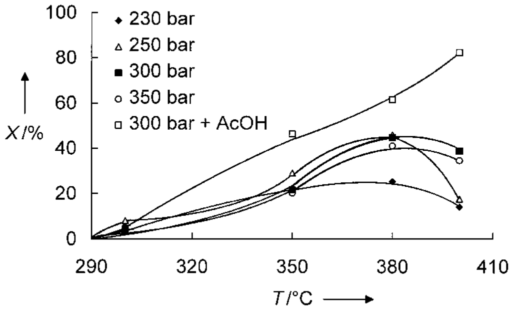


Figure 16. Conversion X in the dehydration of 1,4-butanediol using a mean residence time of 60 s and at four pressures as a function of temperature. The addition of acetic acid accelerates the reaction significantly (compare the filled and open squares).

The dependence of the rate constants on pressure is shown at various temperatures in Figure 17. As expected this is not very marked in the subcritical region. The activation volumes determined from this on the basis of Equation (1) assume positive values (141 cm^{3}mol^{-1} at 300 °C and 94 cm^{3}mol^{-1} at 350 °C) in the subcritical region and negative values (−134 cm^{3}mol^{-1} at 380 °C and −320 cm^{3}mol^{-1} at 400 °C) in the supercritical region. This means that when the pressure is increased the reaction can be retarded in the subcritical region and accelerated in the supercritical region.

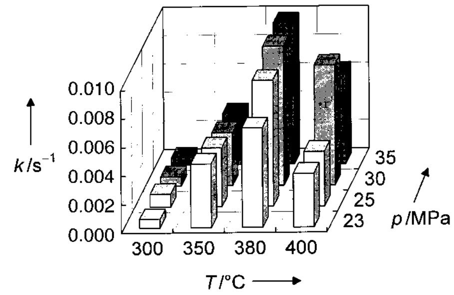
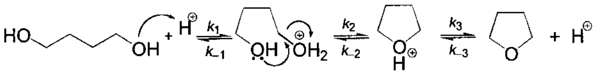


Figure 17. Experimental rate constants for the dehydration of 1,4-butanediol to form THF as a function of pressure and temperature.

The mechanism under conventional conditions has been adequately elucidated (Scheme 7).[83–85] As a result of this ionic mechanism the dissociation constant of the water exercises a powerful effect on the kinetics. In the vicinity of the critical point the pK_w value becomes steadily higher as the density decreases, and so the dissociation of the water steadily declines. As a result, the conversion rates or rate constants fall again when the temperature is increased to 400 °C. In Figure 18 the extent of reaction at 25 MPa is shown as a function of temperature in comparison with the dissociation constant of water.



Scheme 7. Reaction mechanism for the dehydration of 1,4-butanediol to form THF.[83–85]

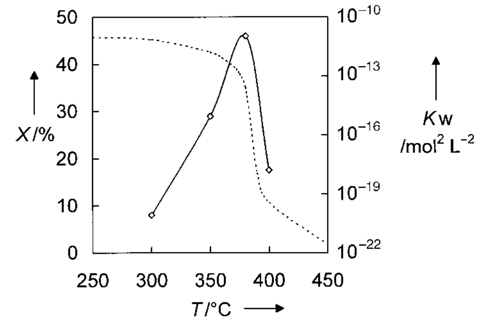


Figure 18. Conversion X in the dehydration of 1,4-butanediol to form THF at 25 MPa with a mean residence time of 60 s as a function of temperature (solid line) in comparison with the K_w value of the water (dashed line, log plot).

8. Summary and Outlook

Supercritical water not only affords great advantages by comparison with conventional solvents from the points of view of ecology, economics, and safety, but it is also a suitable reaction medium particularly on account of its solvent parameters (ionic product and dielectric constant), which can be varied by adjusting the pressure and temperature. Apart from the supercritical wet oxidation already used in practice, chemical syntheses such as hydrolysis, hydration, dehydration, addition and partial oxidation reactions can also be carried out in SCW.

In the subcritical region, where the ionic product of water is relatively high, it was possible to carry out reactions with very high selectivity without the use of a catalyst. Under normal conditions such reactions proceed only with a mineral acid catalyst. Addition of acetic acid in catalytic quantities resulted in acceleration of the reaction for the hydrolysis of ethyl acetate and the dehydration of 1,4-butanediol. In the saponification of ethyl acetate in SCW reaction proceeds preferably by an ionic or nonionic mechanism depending on the conditions. In the supercritical region where the ionic product is relatively low, nonionic mechanisms are evidently preferred. In this region water acts as if it were a nonaqueous solvent.

Studies of corrosion in SCW have shown that specifically in the transition region from subcritical to supercritical the highest specific rates of change in mass occur, this being brought about by the sharp change in the dissociation of water. Despite detectable corrosion silver and copper appear to be suitable as catalysts for partial oxidation reactions in SCW. In corrosion tests using oxygenated aqueous solutions stable oxide layers form on the surface of copper, while in the case of silver removal of material was found due to the instability of the silver oxides formed.

Knowledge of the precise position of the supercritical region is of great interest since here there are no longer any limits to mass transfer. The determination of phase boundary lines for systems of industrial interest, shown here with the example of the water/cyclohexane system, provides accurate information about the phase behavior of the system as a function of the process parameters. Furthermore precise details of densities are needed in order to determine the kinetics of reaction. Calculations carried out on the basis of the density of pure water possibly give rise to incorrect results.

Research in the field of the heterogeneous catalysis of reactions in the moderately supercritical region of fluid water appear highly promising, since practically all the partial steps such as external and internal mass transfer as well as the chemical reaction processes on the surface of the catalyst are positively affected. Future studies in the field of SCW chemistry should also extend to the degradation of biopolymers, especially carbohydrates, since this may well open up a route in which degradation more or less in situ to form monosaccharides with simultaneous change in functionality could be achieved. To carry out precise kinetic measurements on heterogeneously catalyzed reactions, further studies in a continuously operated gradient-free differential loop-type reactor are planned, the focus being on heterogeneously catalyzed partial oxidation reactions.

Despite all the advances there are still unsolved problems such as the identification of suitable reactor and catalyst materials, which in particular must possess outstanding resistance to corrosion in order to open up further types of reactions in chemistry in SCW and to optimize fields which have already been opened up. Applied research in the field of SCW chemistry must not be restricted to synthetic chemistry alone; problems of materials and thermodynamic issues also have to be taken into consideration.

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