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Organic chemistry under hydrothermal conditions*

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Abstract: At elevated temperature, several properties of water are strongly altered compared to what our daily experience tells us: the dielectric constant of water, for example, is reduced, so that water can more easily solubilize organic molecules. In addition, the self-dissociation constant of water is increased (by three orders of magnitude at 250 °C), thus favoring H⁺- and OH⁻-catalyzed reactions. Surprisingly, while room-temperature water and supercritical water (SCW) are well known for promoting organic reactions, the middle temperature range still remains largely unexplored. Therefore, this contribution aims at giving an overview of organic reactions that may be promoted by superheated water.

Keywords: green chemistry; organic chemistry; solvents; water.

INTRODUCTION

Since the early 1990s, we have witnessed a blossoming of articles and books calling for the eve of greener chemical processes. Depending on the authors, "greener processes" meant processes, which are more effective in terms of resources and energy consumption, which emit less polluting species, which employ less toxic products, etc. [1]. These contributions not only announced what we had to aim for, they also gave some directions to achieve this goal. Developing new catalysts to simplify synthetic routes and employing renewable feedstocks are among the most common recommendations. Special attention was also paid to the use of solvents [2].

Indeed, solvents are at the heart of numerous chemical processes. They enable chemical reactions (every second-semester chemistry student knows that nucleophilic reactions, with their polarized transition states, are easier to do in polar solvents like tetrahydrofuran (THF) or, better, acetonitrile, than in nonpolar ones, like cyclohexane, see, e.g., ref. [3]); they control the kinetics of reaction by controlling mass and heat transfers (and, as a result, their selectivity); they even allow one to displace chemical equilibria and "beat" thermodynamics (the synthesis of an imine by reacting an amine with an aldehyde

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under water elimination is equilibrated. When performing this reaction in cyclohexane, the formed water is not soluble in the reaction mixture and drops on the bottom of the vessel; complete conversion is thus achievable, because of water elimination, see, e.g., the use of the Dean–Stark apparatus in ref. [4]). Unfortunately, most solvents are produced using fossil feeds, and their separation from the reaction products or the catalysts and recycling is often expensive and energy-consuming. Therefore, it is not a surprise that Anastas and Kirchhoff devoted one of their famous 12 principles of green chemistry to solvents [1a].

Actually, chemists did not wait until these principles were formulated to start searching for alternative, greener solvents. Further to classical alternatives, such as γ -valerolactone [5] or simply ethanol, two other classes of fluids are at the center of attention today: ionic liquids and supercritical fluids (especially CO₂). However, they both have serious drawbacks: ionic liquids are often either relatively toxic or not biodegradable, they are expensive and require "non-green" synthesis, they are difficult to purify, and due to their very low vapor pressures they cannot be removed by distillation, to cite only few of their disadvantages. The present academic hype for ionic liquids is not in phase with probable applications as solvents in industry [6]. By contrast, supercritical fluids and especially supercritical CO₂ have already proven their industrial relevance. However, they require expensive installations and their applications are still limited to few cases—as it is the case for ionic liquids.

Nevertheless, it is clear that in the next decades many well-known solvents will disappear from the market (halogenated hydrocarbons were only the beginning), and the number of authorized solvents will shrink dramatically. Therefore, there will be an increasing demand for "green" alternatives, even if they are expensive. In this context, superheated water will play an increasing role. In the present paper, we will report on our own fascination for this third "alternative" solvent.

Water is well known to all of us, we use it daily, mainly for its solvating properties, without even thinking about it. From the organic chemist's point of view, standard room-temperature water is an awk-ward solvent. It solubilizes numerous salts and polar or H-bond making molecules, but most molecules of interest for organic chemistry are poorly or not soluble in water. Anyhow, numerous standard organic reactions have been investigated in water below 100 °C [7]. Nevertheless, in numerous such attempts, the question arises whether the reaction actually occurs in water or only in the presence of water [8]. Supercritical water (SCW), on the contrary, does not feature these drawbacks, organic molecules are soluble in this medium and it has been extensively studied as a solvent for organic reactions (we will come back to this point later on). But the pressures and temperatures, required for attaining the super-critical state of water, prevent its large implementation in daily laboratory life (if not in industry).

Luckily, there is a world between those extremes. The physicochemical properties of water are changing rapidly with increasing temperature; at 200 °C, for example, the dielectric constant of water is already less than a third of what it is at room temperature, which means that it is much more of an organic solvent than it used to be. Therefore, the present contribution aims at presenting some recent efforts to employ water between 150 and 220 °C as an advanced solvent for organic chemistry.

For disambiguation purposes, let us state here that we mainly will employ two, in our eyes equivalent, terms in this paper, namely, "superheated water" and "hydrothermal water", defined as liquid water in a temperature range of 100–300 °C under the corresponding autogeneous pressure (thus following Palmer et al. [9]). And we will actually focus on the middle temperature range, between 150 and 220 °C. Other important terms in this topic are supercritical water (SCW, above the critical point) and near-critical water (NCW, approaching the critical point of water). The critical point of water lies at 647.096 K (= 374 °C) and 22.6 MPa, with a density of 322 kg/m³.

ON THE EVOLUTION OF PHYSICOCHEMICAL PROPERTIES OF WATER WITH TEMPERATURE

Before starting the topic of organic reactivity in water, it is useful to review some basic properties of water, which account for its very peculiar behavior. We will concentrate on only a few selected proper-

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ties important for synthesis. For more detailed information, the reader is encouraged to visit the web site of the International Association for the Properties of Water and Steam (IAPWS) [10].

Hydrogen bonding is one of the key factors governing the properties of liquid water. At ambient temperature and pressure, H bonds form an infinite network with a unique structure based on tetrahedral coordination. With increasing temperature and pressure, the relative amount of unbounded, hexagonal structures increases, converging toward the behavior of other simple liquids [11]. This property is well known to physicochemists. With increasing temperature, water also loses its strong hydration power. As a consequence, nonionic surfactants and short-chain amphiphiles (hydrotropes) show the so-called clouding. For a given composition, they undergo phase separation above a certain temperature (the cloud temperature), because their solvation with water molecules is no longer sufficiently high to ensure miscibility [12]. Nevertheless, in water even above the critical point, hydrogen bonding is still present. Here, water tends to form clusters, the structure of which is strongly dependent on temperature and pressure [13].

The **dielectric constant** ε or permittivity describes the ability of a solvent to be polarized by an electric field and is thus a usual marker of solvation properties [9]. A solvent having a high dielectric constant generally dissolves easily ionic species and polar compounds. Solvents with a low dielectric constant dissolve preferentially small organic molecules, while ions form contact pairs [14].

With increasing temperature, the dielectric constant of water decreases (see Fig. 1). At 225 °C, water features a dielectric constant of about 27, which lies between the values of methanol (33) and ethanol (24) at room temperature. As a result, organic molecules are much more soluble in water under hydrothermal conditions. For example, chrysene (a tetracyclic aromatic molecule) is 100000 times more soluble in water at 225 °C as compared to room temperature [15]. In other words, superheated water behaves like a nonpolar solvent, making it an ideal medium for organic synthesis [14]. After cooling down, the initial properties reemerge, and the organic phase can easily be separated from the solvent.



Fig. 1 Temperature dependences of the relative dielectric constant of water at a pressure of 20 MPa. Adapted from ref. [16].

The **ionic dissociation constant**, also called "ionic product of water", is a measure for the amount of autoprotolysis of H₂O molecules into OH⁻ and hydrated H⁺ species. At room temperature, its equilibrium constant K_w is about 10⁻¹⁴ M, which results in the well-known value of pH 7 for neutral water [9]. Initially, the pK_w (equaling the negative decadic logarithm of the K_w value) decreases with increasing temperature, thus accounting for an increased activity of both ionic species (c.f. Fig. 2). Around 250 °C, however, there is a minimum after which the pK_w increases again. Around the critical point, the ionic product varies strongly with temperature and pressure, providing a measure of fine-tuning the catalytic properties of the solvent [14]. It is also important to stress that, as early as 1978, Bussey and

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Fig. 2 Temperature dependence of the dissociation constant of water at 0.1 MPa at T < 100 °C, or p_s (saturated liquid) at T > 100 °C. Adapted from ref. [10].

Mesmer have evidenced that the addition of "inert" salts to superheated water has a strong impact on its dissociation constant [17].

Other important factors to change the rate constants of reactions are the transport characteristics of a solvent. They consist of parameters such as viscosity, heat capacity, diffusion coefficients, and density [18]. In general, they alleviate reactions with increasing temperature; for exact values, the reader is referred to the corresponding literature [10]. Here we shall only mention that by controlling the density around the critical point, a lot of other variables can be controlled to a high extent [18].

SOME ASPECTS OF THE USE OF NEAR-CRITICAL OR SUPERCRITICAL WATER IN ORGANIC CHEMISTRY

As early as 1913, it has been suggested that, in nature, hydrothermal reactions were responsible for the formation of fossil fuels, especially coal [19]. And even previous to the formation of coal deposits, the prebiotic synthesis of the first organic molecules on Earth, the emergence of life, probably took place in a hydrothermal environment [20]. Similar conditions are still found at hydrothermal vents in the deep sea. Despite that, organic synthesis in high-temperature water was not popular until the 1980s. Numerous different organic reactions have been realized since, and some good reviews are available to summarize these developments [18,21]. Interestingly, most of these reports focus on relatively harsh reaction conditions, mainly above 250 °C. It is not the goal of this paragraph to give a detailed overview of these reports but to summarize, for comparison, the main type of organic reactions described in SCW.

These reactions may be ordered into the following four main classes:

- eliminations (dehydration, decarboxylation...)
- condensations (alkylation, aldol reaction, Claisen–Schmidt condensation...)
- additions (Diels-Alder reaction, Heck reaction, and other coupling reactions...)
- redox reactions (hydrogenation, dehydrogenations, oxygen addition...)

Table 1 gives some examples of such reactions in SCW and NCW.

Reaction type	Example	Temperature range (°C)	Yields (%)	Ref.
Dehydration	он он	360	75	22
Alkylation (Friedel–Crafts type)	OH + ^t BuOH → ^{OH} t ^t Bu	275	20	23
Condensation (Aldol type)		250	24	24
Condensation (Diles-Alder type)	+ OMe CO ₂ Me	375	86	25
Oxidation	$ \bigcirc \circ $	375	60	26

 Table 1 Some examples of organic reactions occurring in SCW.

ORGANIC REACTIONS IN SUPERHEATED WATER

As previously stated, hydrothermal conditions are familiar to materials scientists. Indeed, materials as important as zeolithes [27], oxide nanoparticles [28], or mesoporous oxides [29] are often synthesized under hydrothermal conditions. More recently, even hybrid or purely organic materials have been successfully synthesized under such conditions, for example, metal organic frameworks [30] or hydrothermal carbon [31]. On the contrary, water in the low hydrothermal temperature range (between 150 and 220 °C) constitutes a kind of organochemical no-man's-land, and only a few studies report on the use of superheated water to promote organic reactions.

Organic reactions in pure water and brines

As already mentioned by Katritzky and co-workers [32], pure water at "moderate" temperatures (up to 250 °C), does not strongly impact unactivated organic molecules. The addition of "catalysts" is needed to achieve a measurable degree of reactivity. This part of our work was devoted to investigating a very simple catalyst: sodium chloride.

Model reactions in superheated water [33]

Based on the above-mentioned literature reports on organic reactivity in SCW, we anticipated that the dehydration of alcohols was the best suited reaction to start investigating the effect of catalysts under hydrothermal conditions. We thus selected a limited range of activated alcohols, which were heat treated in water at 180 °C for 16 h. Figure 3 gives an overview of our observations and highlights that:

• In the case of 1-phenylpropan-1-ol (Fig. 1A), the classically proton-catalyzed dehydration reaction is observed; as was expected (cf. part 2), superheated water can behave as an acid.

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- More complex reactions, like pinacolic rearrangements (Figs. 1D,E) or aldol condensations (Fig. 1C), may also occur. This already opens a broad field of applications for superheated water in organic chemistry.
- Although the employed substrates may be sensitive to oxidation, no oxidation products were detected. This confirms the assumption by Antal and co-workers [34] that only heterolytic processes (and no radical processes) are at work under these conditions.



Fig. 3 Reaction schemes of some activated alcohols in superheated water.

Specific salt effects on these reactions

As was expected, despite some very favorable examples, most conversion rates remained relatively low and we were looking for some catalysts to enhance the obtained yields. As previously mentioned, it was shown more than 30 years ago that the addition of NaCl to water further increased its dissociation constant at higher temperature. If this observation is true and if our reactions are really proton-catalyzed, then the addition of such a simple salt as NaCl, must accelerate our organic reactions. Table 2 compares the yields obtained in the reactions described in Fig. 3, in pure water and in 1 M NaCl. As can be seen in all cases, the use of brine as a reaction medium resulted in a sensible yield increase (with the exception of pinacol, which already provided the rearrangement product to 98 % in pure water), confirming our hypothesis. In order to further investigate this salt effect in organic chemistry, we selected phenylpropan-1-ol as a model molecule and tested a broad range of ion pairs. These tests evidenced that the outcome of the reaction was barely impacted by the nature of the cations and that the nature of the anion played a predominant role. Figure 4 shows the yields of phenylprop-1-ene (the major dehydration product of phenylpropan-1-ol) obtained with a series of sodium-based salts as a function of the pK_a of the anions. The correlation between the pK_as and the yields is striking. While anions corresponding to strong acids can promote the dehydration reaction, the ones corresponding to weak acids block it. This is evidence that ion pairs can formally act as acids or as bases at high temperature in water and are very promising for the design of tailored synthetic reactions in superheated water.

Entry	Starting compound	Main product	Yield of product (%)	
			Pure water	1 M NaCl
1	ОН	$\bigcirc \checkmark$	75	98
2	ОН	\bigcup	53	70
3	ОН		21	64
4	он	°	98	98
5	ОН	C C	73	89
	1.0 - T	I		

Table 2 Comparison of some organic reactions at 180 $^\circ$ C in pure water and 1 M NaCl solution.



Fig. 4 Effect of various ion pairs on the dehydration of 1-phenylpropanol. Adapted from ref. [33].

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One example of such tailor-made synthesis under hydrothermal conditions has been provided by Kopetzki and Antonietti. Indeed, these authors nicely evidenced that sulfate anions can be employed as temperature-switchable bases to promote the transfer hydrogenation of levulinic acid with formic acid [35].

Organic reactions in superheated diluted acids [36]

From the above-mentioned section ("Organic reactions in pure water and brines"), it is clear that hydrothermal water is a very promising medium for organic chemistry. It was thus tempting to try pushing the reactivity a bit forward to test the limits of this solvent. In Fig. 3C, one witnesses the condensation of phenylethandiol to a dimer via a formal aldol condensation. A natural question is then to determine whether or not it is possible to go further and force the diol to react to a trimer, which might be triphenyl benzene as depicted in Scheme 1. Unfortunately, all our attempts to get more than a dimer in water or brines failed. We thus decided to investigate this reaction in the presence of diluted acids.



Scheme 1 A possible pathway for 1-phenylethan-1,2-dioltrimerization.

As depicted in Scheme 2, this attempt also failed, but at least a new type of reactivity came to light. Indeed, in the presence of $0.05 \text{ mol}\cdot\text{L}^{-1}$ of HCl, the main product of the reaction became 3-phenylnaphthalene. This product originates from a formal intramolecular Friedel–Crafts addition of the formed aldol condensation product.



Scheme 2 Reaction of 1-phenylethan-1,2-diol in diluted HCl at 180 °C for 16 h.

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Organic chemistry in superheated water

This discovery prompted us to investigate the addition of alcohols to phenol derivatives in superheated diluted acids (Scheme 3). Indeed, the use of alcohols as alkylation agents has received much attention in recent years because they are much greener than usual halides, especially because they release only water as a byproduct [37]. In addition, phenol was selected because of its good solubility in water and because its alkylation with standard catalysts is often hindered by its acting as a ligand for the employed metals. In addition, the alkylation of phenol with activated alcohols in SCW has already been investigated (cf. Table 1). Figure 5 shows how the yield of monoalkylation product evolves with increasing acid concentration. As can be seen at concentrations as low as $0.03 \text{ mol}\cdot\text{L}^{-1}$, the conversion of benzyl alcohol is almost complete. The yield in monoalkylation products exceeds 60 %. This approach could be extended to a broad range of phenol derivatives and activated alcohols [36].



Scheme 3 Friedel–Crafts-type alkylation of phenol with benzyl alcohol.



Fig. 5 Evolution of the benzylalcohol conversion and the yield in monoalkylated Friedel–Crafts products as a function of HCl concentration at 180 °C for 16 h. Adapted from ref. [36].

Application to biomass conversion

Anticipating a possible shortage in fossil resources, organic and materials chemistry is more and more looking at biomass as a possible feed [38]. Unfortunately, most chemical processes are designed for fossil feeds and new processes are to be designed to cope with the numerous drawbacks of biomass and its derivatives, namely,

- variability,
- high moisture, and
- high heteroelement contents.

The promising initial results obtained in hydrothermal organic chemistry resulted in a strong interest for superheated water as a medium to upgrade biomass.

Hydrothermal carbonization

The most successful application of hydrothermal organic chemistry to biomass is probably hydrothermal carbonization (HTC). HTC involves contacting biomass with a certain amount of water at temperatures between 150 and 250 °C mostly under autogenic pressure. The HTC was first described by Bergius in 1913 [19], and it has enjoyed a renewed interest since 2005 [39].

Due to the chemical complexity of biomass and its constituents, many chemical transformations take place during the treatment of cellulose under HTC. Just as an example, one may consider how many reactions have been evidenced in the previous sections on a relatively simple diol-like phenylethandiol (see the section "Organic reactions in super-heated diluted acids") and how complex these reactions may become with a **polyol**, like glucose. According to both investigations by Fuertes [40] and Baccile [41], hydrothermal carbons produced from sugars or cellulosic biomass at temperatures below 180 °C are mainly constituted of a polycondensed furanic network, while carbons produced at higher temperatures feature distinct polyaromatic properties. A schematic mechanism of formation of hydrochar is depicted in Scheme 4. In a first step, cellulose chains hydrolyze into different oligomers (including glucose), which dehydrate and fragment to form furanic and aromatic derivatives. In a last step, various types of condensation reactions take place to yield first polyfuranic derivatives and, at last, hydrochar. It is worth stressing here that most single reactions assumed by these authors (dehydrations, Friedel-Crafts-type, and aldol condensations) have been evidenced on model molecules (c.f. sections "Organic reactions in pure water and brines" and "Organic reactions in super-heated diluted acids").

Besides the academic interest of these processes, several applications of HTC have been suggested, namely,

- the synthesis of porous materials, which may be useful for chemical separation or gas storage [43],
- the preparation of catalysts [39d,44],
- the preparation of electroactive phases [45],
- soil amendment [46], and
- biomass enhancement for solid fuel production [47].

Glycerol

Biodiesel is produced from natural triglycerides (natural oils in particular). These triglycerides are transesterified with methanol, yielding the needed fatty acid methyl esthers and glycerol. Glycerol itself is an important chemical commodity, but unfortunately the produced bioglycerol is polluted with water and salts and its refining is very expensive. Processes are thus needed to convert unpurified glycerol into useful products. Here again, SCW has already been investigated to promote the conversion of glycerol into acrolein, and good yields were obtained (c.f. Table 1 and ref. [22]). On the contrary, the direct hydrothermal treatment of glycerol resulted mainly in low-value carbonization product and was thus not suited. Recent works, however, have shown that it was possible to effectively convert glycerol into



Scheme 4 Mechanism of formation of hydrochar from cellulose by HTC (adapted from ref. [42]).

propan-1,2-diol, both in gas and aqueous phase (Scheme 5) [48]. We decided to focus on the latter molecule.

Like in the section "Organic reactions in super-heated diluted acids", pure water or brines did not promote any reaction of propandiol at temperatures below 230 °C, but diluted acids proved to be useful. As shown in Scheme 6, a treatment at 180 °C in 0.05 M HCl yielded 25 mass % of trimerization products. The overall yield could even be improved by recycling the reaction medium and limiting starting material hold-up.

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Scheme 5 Hydrogenolysis of glycerol into 1,2-propanediol.



Scheme 6 Trimerization of 1,2-propanediol in hydrothermal acids.

Cellulose

Cellulose is a very abundant biomass product. It is already widely used for the production of paper and packaging. It is also a source of C₆ sugars and may become a major source of second-generation biofuels, especially bioethanol [49]. Alternatively, a report of the U.S. Department of Energy (DoE) suggested that cellulose may easily be transformed into ethyl levulinate (Scheme 7), of which up to 10 mass % may be added to gasoline without impeding the performance of the engines [50]. Actually, the ethyl levulinate may be produced under solvothermal conditions (in a mixture of acidic water and ethanol). In an attempt to extend the scope of this reaction, we investigated the synthesis of ethyl levulinate both from cellulose and unpurified biomass. After a series of optimization tests on pure glucose we decided to employ 0.5 M HCl as the acid and to mix it with ethanol in a volumetric ratio of 3:7. After 16 h of reaction at 180 °C we obtained 87 % of ethyl levulinate. These reaction conditions were then employed to convert the cellulose contained in various types of crude biomass. Figure 6 dispatches the obtained yields of ethyl levulinates expressed as mol % of the leachable hexoses. As can be seen, there is no clear trend in the results. For example, different parts of giant reed (ArundoDonax) featuring very similar components of leachable hexoses yielded sensibly different amounts of ethyl levulinate (only 46 % for the leaves compared to 59 % for the bottom of the plant). This is very surprising, and we suspect that parasite reactions of other components account for this observation. Anyhow, softwood chips (pinewood) behaved well and yielded up to 70 % of ethyl levulinate.



Scheme 7 Conversion of cellulose into ethyl levulinate.



Fig. 6 Correlation between the amount of hydrolyzable hexose and the ethyl levulinate yield in various biomass feeds.

CONCLUSION

The aim of this contribution was to highlight several achievements in the use of superheated water as a medium for organic synthesis. But more important is what still remains to be done. From the present account, it appears that the most important needs are

- to develop base-catalyzed reactions in superheated water (employing the mentioned specific salt effects),
- to precisely understand the role of "inert" salt in hydrothermal organic chemistry in their impact on hydrothermal biomass transformation, and
- to explore the potential of transition-metal-based catalysis in superheated water.

We are confident that these three questions open the way to new, more effective syntheses and processes for the valorization of biomass and fine chemical production.

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