

Organic reactions in high-temperature and supercritical water*

Joan Fraga-Dubreuil and Martyn Poliakoff‡

The School of Chemistry, University of Nottingham, Nottingham NG7 2RD, UK

Abstract: This paper describes various examples of organic reactions carried out in high-temperature water (HTW) that have been performed at the University of Nottingham using either batch-type reactors or continuous-flow systems. Homogeneously and heterogeneously catalyzed partial oxidations of aromatic compounds, in situ hydrogenations, heterocyclic reactions, hydrolysis (HYD), saponification (SAP), and deuteration reactions are presented.

Keywords: high-temperature water; partial oxidation; in situ hydrogenation; heterocycle synthesis; hydrolysis.

INTRODUCTION

The research of alternative, environmentally more acceptable processes for the manufacture of chemicals is nowadays fundamental [1]. There is an increasing concern about the impact that chemicals have on the environment, and there is no alternative for modern industry but to investigate “greener” approaches to conventional chemical processes. The application of green chemistry in industry is perhaps the main challenge for researchers, who are often limited to academic developments.

The use of high-temperature water (HTW) as a benign medium for chemistry is particularly attractive because of its unique properties [2]. Water becomes a supercritical fluid above 374 °C and 221 bar (22.1 MPa), and it can be a useful replacement for organic solvents, not only because it is cheap, naturally abundant, and nontoxic but also because, near and above the critical point, its physicochemical properties (dielectric constant, ionic product, density, degree of hydrogen bonding, etc.) can be finely “tuned” with pressure and temperature. This means that the chemical environment can be modified without changing the solvent. Also, there are cases in which water can simultaneously play the role of solvent, reactant, and catalyst.

Recently, our group and others have reported studies on the continuous hydrothermal synthesis of metal oxide nanoparticles [3]. A wide range of organic reactions have also been reported [4] which show that the HTW environment offers many opportunities for cleaner synthesis. However, there are relatively few papers reporting selective reactions in HTW compared to the large number of reports on total oxidations [5], destruction of organic wastes [6], or conversion of biomass for hydrogen production [7].

In this paper, we review some examples of organic reactions in HTW, particularly, continuous reactions, that have been performed by our group at the University of Nottingham. This includes (i) selective partial oxidations of methyl aromatics to their corresponding carboxylic acids; (ii) the heterogeneously catalyzed oxidation of benzoic acid (BA) to phenol; (iii) in situ hydrogenations of organic

*Paper based on a presentation at the Second International Symposium on Green/Sustainable Chemistry, 10–13 January 2006, Delhi, India. Other presentations are published in this issue, pp. 1971–2050.

‡Corresponding author: E-mail: Martyn.Poliakoff@nottingham.ac.uk

substrates using either Zn or HCO_2X (H, Na, NH_4) as a source of hydrogen; (iv) heterocyclic reactions (synthesis of quinolines, indoles, benzimidazoles); (v) hydrolysis (HYD) (or saponification (SAP)) of esters and nitriles; and (vi) deuteration of aromatic compounds. We concentrate on the overall results and their context. Full experimental details can be found in the references cited.

RESULTS AND DISCUSSION

Continuous selective oxidations

Oxidation of methylaromatics

Homogeneously catalyzed selective oxidations of diverse alkylaromatics (xylenes and polymethylbenzenes) have been investigated by our group using a continuous-flow reactor (Fig. 1).

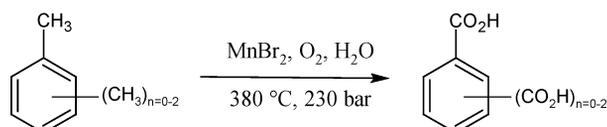


Fig. 1 Homogeneously catalyzed oxidation of methylaromatics in HTW.

This process offers a route to the production of bulk chemicals such as terephthalic acid that is potentially cleaner than traditional methods which generate significant waste and require large volumes of acetic acid as solvent [8]. We have reported that different methylaromatic compounds [1,4-dimethylbenzene (*p*-xylene), 1,3-dimethylbenzene (*m*-xylene), 1,2-dimethylbenzene (*o*-xylene), 1,3,5-trimethylbenzene (mesitylene), and 1,2,4-trimethylbenzene (pseudocumene)] can be aerobically oxidized in supercritical water (scH_2O) using manganese(II) bromide as the catalyst to give the corresponding carboxylic acids in a continuous mode over a sustained period of time in good to moderate yields [9] (Table 1).

Table 1 Yields and selectivities of acids obtained during partial oxidation of different methylaromatics [8–10].

Substrate	Main product ^a	Yield (%) ^b	Selectivity (%) ^b
<i>o</i> -Xylene	OPA	52	94
<i>m</i> -Xylene	IPA	66	97
<i>p</i> -Xylene	TA	90	95
Ethylbenzene	BA	68	96
Mesitylene	TSA	78	93
Pseudocumene	TMA	50	80
C_8 mixtures ^c	OPA/IPA/TA/BA	45–66	93–95

^aOPA: *ortho*-phthalic acid, IPA: *iso*-phthalic acid, TA: terephthalic acid, BA: benzoic acid, TSA: trimesic acid, TMA: trimellitic acid.

^bYield and selectivity of the main product calculated by HPLC.

^cE.g., a mixture of ethylbenzene (45 %), *ortho*- (13 %), *meta*- (24 %), and *para*- (18 %) xylenes.

In this reaction, a mixture of H_2O and O_2 is contacted in a 3-way mixer under supercritical conditions with separate streams of pure organic substrate and a cold solution of MnBr_2 using a continuous-flow reactor, which has been described previously [8,9].

A particular feature of these oxidations is that very low levels of partially oxidized intermediates (i.e., toluic acid and benzaldehydes) were detected for the dimethylbenzenes and mesitylene reactions.

By fine-tuning pressure and temperature, scH_2O becomes a solvent with physical properties suitable for single-phase oxidation since both organic substrate and oxygen are soluble in scH_2O . Aromatic acids produced by the loss of one methyl group were detected in all of these reactions, i.e., 3–6 % BA formed during the oxidation of the dimethylbenzenes. Part of this loss is thought to be due to thermal decarboxylation, and we have monitored this via Raman spectroscopy [9].

It can also be seen from Table 1 that a mixture of xylenes, for instance, the unseparated C_8 refinery mixture (*o*-xylene 13 %, *m*-xylene 24 %, *p*-xylene 18 %, ethylbenzene 45 %), can be simultaneously oxidized in scH_2O in a continuous system to a mixture of the corresponding carboxylic acids in moderate yields (45–66 %), despite the differences in reactivity of the xylene isomers in conventional oxidation [10]. The supercritical single-phase environment and the effect of higher temperatures increase the reaction rate for each of these oxidation reactions and thus lower the reactivity differences between the C_8 compounds. This process could potentially reduce the overall energy required for the oxidation of the separated xylenes and simplify the downstream purification to a crystallization process. A method for separating the products from the oxidation of mixed xylenes using selective crystallization solvents has been described in a patent [11]. This is of potential commercial importance, because the purification process can be as expensive as the reaction of oxidation. Furthermore, the direct oxidation of C_8 mixtures could avoid the need for the upstream separation of the xylene isomers.

These reactions are interesting because conventionally the presence of H_2O lowers the catalytic activity of MnBr_2 at lower temperatures. Partenheimer and coworkers [12] have recently shown that there is a strong structural similarity of metal/bromide coordination compounds in the active oxidation solvents, acetic acid, and scH_2O . Extended X-ray absorption fine structure (EXAFS) and X-ray absorption near-edge structure (XANES) spectroscopies were used to identify the first-shell coordination structure about Mn(II) and Br^{-1} ions, showing that they exist as contact ion pairs in supercritical water. The Mn(II) structure changes from octahedral at ambient conditions to tetrahedral at supercritical conditions. This change greatly promotes the Mn–Br bonds and as water becomes more akin to a low polarity solvent like acetic acid (or acetone), the MnBr_2 catalyst becomes active. This explains why water can act as an effective aerobic oxidant solvent in supercritical conditions.

The use of HTW offers potential cost advantages through enhanced energy recovery, due to a higher process temperature and the exothermicity of these reactions. Compared to the existing industrial method, the supercritical water process has the potential for a substantial reduction in waste (by-products from acetic acid and CO_2 production) and offers economical advantages resulting from more selective and faster reaction. Dunn and Savage have recently evaluated the capital cost and the energy consumption of the HTW process, in particular for terephthalic acid synthesis [13]. They concluded that on a large scale, the HTW process could be less energy intensive, more environmentally friendly, and of a similar cost as the traditional method performed at lower temperature.

Oxidation of benzoic acid to phenol

The oxidative decarboxylation of BA to phenol (the Dow Phenol Process) has been studied in HTW using a continuous-flow system over various metal oxide heterogeneous catalysts [14]: NiO, CuO, Carulite[®], MnO_2 , and Al_2O_3 . Excellent selectivities (>99 %) and good yields for phenol (up to 70 %) were achieved (Table 2).

Table 2 Effect of the catalyst on phenol yield and selectivity in HTW [14].

Catalyst ^a	<i>T</i> (°C)	<i>p</i> (MPa)	Phenol yield ^c (%)	Phenol selectivity ^c (%)
NiO	360	25	12	23
CuO	360	25	13	>99
CuO	340	20	28	>99
Carulite 300 ^b	340	14	70	95
Carulite 300	350	20	50	>99
Carulite 100 TR	340	14	27	>99
MnO ₂	320	20	0	–
Al ₂ O ₃	350	20	1.5	>99

^a6 g of catalyst were used in all experiments except for the experiment performed at 350 °C with Carulite 300 where 8.3 g of catalyst were used.

^bAddition of 18 % molar NaOH.

^cOptimum phenol yield and selectivity.

The reaction conditions were optimized by varying the temperature, the pressure, and the effect of O₂. Experiments were carried out for sustained periods in order to study the catalyst deactivation. Carulite 300 was the most effective with a good activity/robustness over time-on-stream. Commercially available Carulite catalysts (Carus Chemicals, Inc. [15a]) are composed of 40–60 % MnO₂ and 1–3 % CuO, supported on X-ray amorphous Al₂O₃. They are relatively stable in sub- and supercritical water [15b].

In each run, a lag-time was observed before obtaining optimum phenol yield, then the phenol yield decreased due to catalyst deactivation (Fig. 2). The metal oxide was thought to be reduced over time, and reoxidation of the catalyst could be achieved by supplying oxygen to the system.

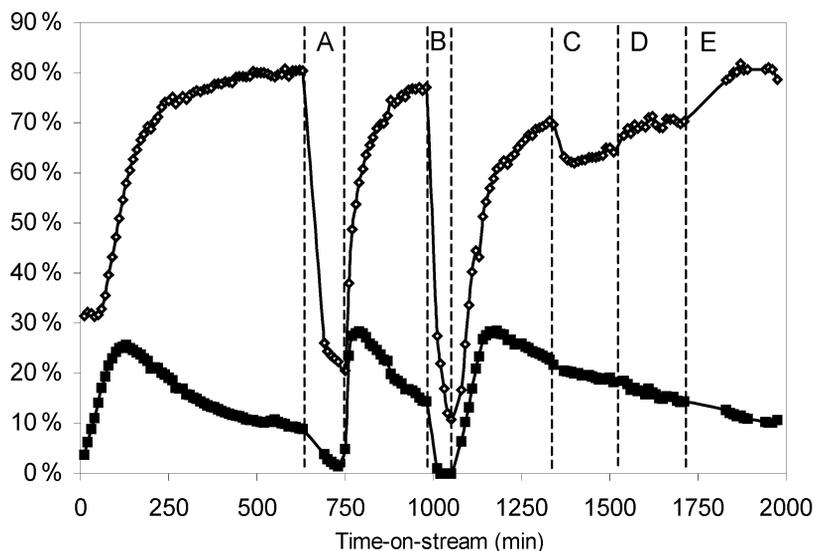


Fig. 2 The continuous oxidation of BA to phenol over Carulite 300 (6 g) at 350 °C and 20 MPa (modified from ref. [14]). Number of O₂ equiv pumped in the reactor: (A) 11.2; (B) 112; (C) 0.9; (D) 0.45; (E) no O₂. It can be seen that the catalyst can be reactivated in presence of O₂ for several cycles without changing its activity. Simultaneous feed of O₂ and BA decreases the phenol yield. ■ Phenol yield, ◇ BA recovery.

During the period of reactivation of the catalyst, it was found that the catalyst was very active for total oxidation of the organic material, but when the oxygen feed was stopped, similar phenol yields and selectivities were obtained over several cycles. Overall, HTW shows considerable potential as a reaction medium for this process. The extension of this chemistry to the synthesis of other phenolic compounds from diverse aromatic carboxylic acids may well be possible.

Reduction of organic substrates in HTW

Reduction of nitroarenes to anilines

A new method for the preparation of anilines by reduction of the corresponding nitroarenes using Zn in H₂O at 250–300 °C has been described [16] (Fig. 3). The reaction involves reduction of H₂O by Zn to generate H₂, followed by hydrogenation of the NO₂ group catalyzed by residual traces of Zn. It was observed that the procedure was efficient enough to reduce sterically hindered 2-nitro-*m*-xylene and is chemoselective for the reduction of NO₂ groups in 1-chloro-2-nitrobenzene and 1-nitro-3-vinylbenzene. Good yields (up to 97 %) and conversions of the starting nitroarene (up to 100 %) were obtained using a batch reactor with an appropriate amount of Zn (3–10 equiv) in less than 2.5 h, depending on the nature of the organic substrate. Selected results are presented in Table 3. In most of the cases, reactions can be carried out using a stoichiometric amount of Zn (3:1, Zn:nitroarene) for 2.5 h or less; however, using a small excess of Zn can reduce the reaction time to just 10–20 min.

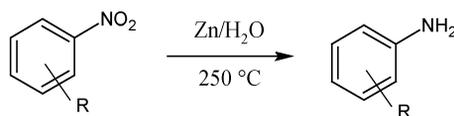


Fig. 3 Reduction of nitroarenes to anilines using Zn in HTW.

Table 3 Reduction of nitroarenes to anilines with Zn/H₂O at 250 °C [16].

R	Zn:org	Time/h	Yield ^a (%)	Conv. (%)
H	9:1	0.3	97	96
2-Me	3:1	2.5	85	85
2,6-di-Me	6:1	2.5	90	55
2-Cl	3:1	1.5	88	93
2-Br	3:1	0.3	57	72
2-I	3:1	0.1	87	86
4-MeO	6:1	2.0	70	100
3-vinyl	10:1	0.2	90	77

^aGravimetric yield calculated on reacted nitroarene.

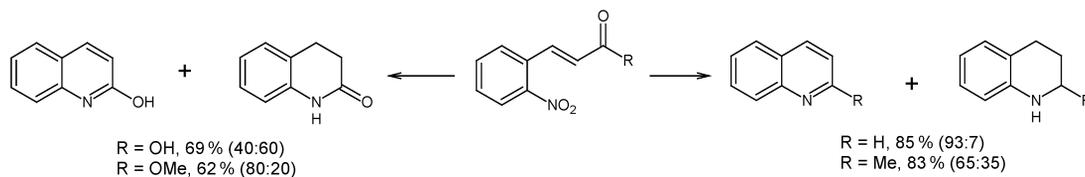
Synthesis of quinolines and indoles

As an extension of the nitro-reduction described above, quinoline and indole derivatives have been prepared by reduction of suitably functionalized *o*-nitroarenes with Zn powder in H₂O at 250 °C [17]. The process involves the reduction of the nitro group to an amino group followed by intramolecular cyclization with a carbonyl or alcohol moiety. The yield of hydroquinoline depends on the nature of the carbonyl moiety of the nitroarene. Using this HTW method, good yields of quinoline and indole derivatives were achieved (62–85 % and 80–91 %, respectively) (Fig. 4).

This single-step procedure is clean and efficient because it avoids the use of solvents or acid media, which facilitates the work-up of the reaction (the need for a neutralization step is eliminated).

Only a few minutes of heating were required to drive the reaction to completion. Therefore, it has considerable potential for use in heterocyclic synthesis.

Quinolines



Indoles

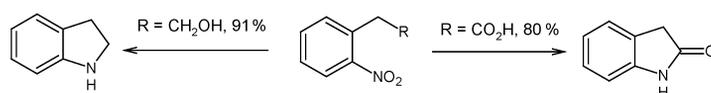


Fig. 4 Reduction of nitroarenes with Zn (Zn:org 4:1) in H_2O at $250\text{ }^\circ\text{C}$ in a high T/p batch reactor [17].

In situ generation of H_2

The thermal decomposition of HCO_2X ($\text{X} = \text{H}, \text{Na},$ or NH_4) has been studied in HTW and used as a source of H_2 for the continuous hydrogenation of aromatic and cyclic aldehydes, ketones, and nitroaromatics in HTW [18]. The hydrogenation reactions can be performed in the same apparatus as has previously been reported for selective oxidation in HTW [8–10]. Pure organic substrate was pumped into the reactor and reacted with H_2 in HTW at pressures between 15 and 20 MPa and temperatures between 250 and $300\text{ }^\circ\text{C}$.

On the laboratory scale, this approach is a simple, convenient, and safe method to carry out hydrogenation reactions. It gives a simpler control of the H_2 -flow rates, especially in small-scale apparatus, where very low flow rates are required. The other advantage that offers this process is that it avoids the use of a compressor, which is especially critical for hydrogen in terms of safety and equipment costs (a compressor is needed because the pressures of sCH_2O experiments are greater than the pressure in a standard gas cylinder).

Table 4 Hydrogenation of various organic substrates in HTW using HCO_2X as a source of H_2 [18].

Substrate	Product	p (MPa)	T ($^\circ\text{C}$)	X	Yield ^a (%)
Nitrobenzene	Aniline	15.0	300	H	75
Nitrobenzene	Aniline	20.0	300	Na	98
Benzaldehyde	Benzyl alcohol	15.7	247	Na	65
Benzaldehyde	Benzyl alcohol	15.0	250	NH_4	94
Cyclohexanone	Cyclohexanol	15.5	250	Na	28

^aYield of product calculated by HPLC or GC (cyclohexanol).

Synthesis of benzimidazoles

The synthesis of benzimidazoles in HTW has been described using a high-pressure mini-autoclave [19]. These compounds were prepared from 1,2-phenylenediamine and various carboxylic acids via double dehydration and intramolecular cyclization (Fig. 5). A systematic study of the reaction parameters (tem-

perature, pressure, reaction time, and concentration) in the synthesis of 2-phenylbenzimidazole as a model compound was performed in order to tune the solvent properties of water and to optimize the benzimidazole yield. The best yield was achieved at 350 °C and 20 MPa (90 %). The effect of the temperature on the initial rate of the reaction was investigated and monitored by in situ UV–vis spectroscopy [19]. The optimized conditions were applied to other substituted imidazoles by using various mono and dicarboxylic acids (Fig. 5, Table 5).

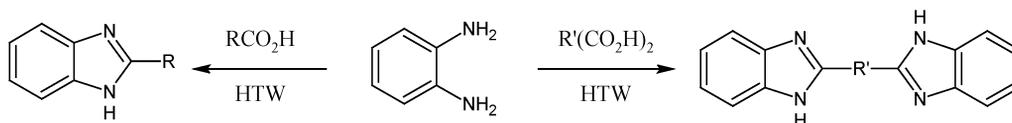


Fig. 5 Synthesis of substituted benzimidazoles from 1,2-phenylenediamine [19].

Table 5 Effect of the nature of the carboxylic acid on the yield of (bis-)benzimidazole in HTW.

R	Yield (%) ^a	R'	Yield (%) ^a
H	79	–	30
Me	42	(CH ₂) ₂	68
<i>i</i> Pr	72	<i>p</i> -C ₆ H ₄	70
<i>t</i> Bu	31	<i>o</i> -C ₆ H ₄	62
CH ₂ Ph	92		
Ph	90		

^aYields obtained gravimetrically (see conditions in ref. [19]).

This reaction is clean because we not only replace volatile organic solvents with water but also eliminate the use of acidic catalysts and subsequent neutralization as required in conventional synthesis. Some of the products have crystallized in situ and been characterized by X-ray diffraction without the need for further purification.

Hydrolysis

Hydrolysis and saponification of methyl benzoates

The HYD and SAP of methylbenzoates in both water and slightly alkaline solution (2 % KOH) at high temperature (200–375 °C) has been studied (Table 6, Fig. 6) [20]. Using this method, partial HYD or quantitative SAP of sterically hindered and *p*-substituted methyl benzoates was achieved in 30 min.

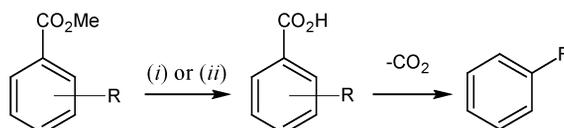


Fig. 6 HYD or SAP of methyl benzoates followed by decarboxylation. (i) HYD: HTW, 250–300 °C; (ii) SAP: 2 % KOH/HTW, 200–375 °C.

Table 6 Conversion of methyl benzoates and yields of corresponding acids after 30 min in HTW [20].

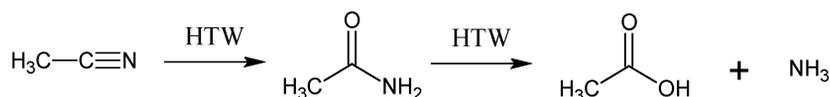
R	Conv. (%) HYD ^a	Conv. (%) SAP ^b	Yield (%) HYD ^a	Yield (%) SAP ^b
2,4,6-tri-Me	21	60	20	57
2,4-di-Me	30	81	28	79
H	60	100	59	98
<i>p</i> -NO ₂	74	100	66	88
<i>p</i> -CF ₃	65	100	64	98
<i>p</i> -OMe	56	92	46	90
<i>p</i> -NH ₂	62	100	7	84

^a*T* = 250 °C.^b*T* = 200 °C, except for R = 2,4,6-tri-Me and 2,4-di-Me (*T* = 250 °C).

Methyl 2,4,6-trimethylbenzoate and methyl *p*-aminobenzoate can also be selectively decarboxylated or hydrolyzed by changing the conditions of the reaction medium, temperature, and/or pH. The nucleophilicity of diluted alkaline solution at high temperature is greatly enhanced. This was demonstrated by the quantitative HYD of the sterically hindered ester (R = 2,4,6-tri-Me) at 300 °C and to our surprise the HYD of methyl *p*-(trifluoromethyl)benzoate (R = CF₃) to terephthalic acid at 375 °C. Although the formation of HF is potentially dangerous in this context, the conversion of CF₃ group to CO₂H clearly shows the efficiency of this method of HYD.

Hydrolysis of acetonitrile and spectroscopic monitoring of the reaction

The HYD of CH₃CN in near-critical water was previously reported [21] and has also been studied by our group [22]. The reaction is successfully performed without any added catalyst and involves the formation of CH₃CONH₂ as an intermediate, and gives CH₃COOH as the final product:



This pathway was monitored via online Raman spectroscopy, up to 350 °C at 300 bar (Fig. 7). Using a unique miniature high-pressure and -temperature spectroscopic cell [23], in situ quantitative measurements have allowed the pseudo-first-order rate constants of the reaction to be calculated from 275 to 350 °C. The rate constant was about 30 times greater at 350 °C than at 275 °C. From these results, the Arrhenius plot allowed the activation energy *E*_a of the reaction to be determined, 131 ± 9 KJ·mol⁻¹. The effects of temperature, pressure, density, dielectric constant, ionic product of water, and initial CH₃CN concentration on the reaction rate were also studied.

No other products were detected in the effluent. Water simultaneously plays the role of solvent, reactant, and acid catalyst, whereas the reaction also shows an autocatalytic effect, due to the presence of acetic acid that accumulates in the system as the reaction progresses. The HYD of nitriles is of interest since C≡N groups are commonly found in many commercial products, so they are major constituents of waste streams. It is therefore important to know the kinetics of these reactions for the treatment of industrial effluent.

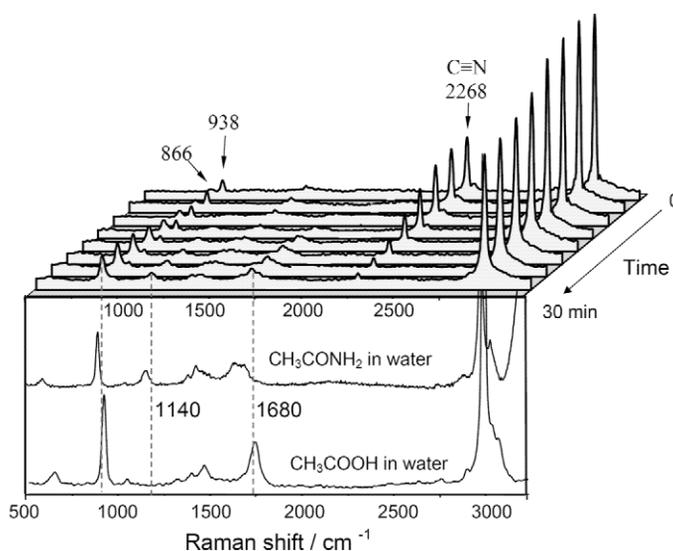


Fig. 7 Raman spectra of CH_3CN in water at $300\text{ }^\circ\text{C}$ and 300 bar , showing the HYD of the $\text{C}\equiv\text{N}$ group (modified from ref. [22]). We can see that the $\text{C}\equiv\text{N}$ vibration peak at 2268 cm^{-1} decreases gradually over 30 min reaction time. For comparison, standard spectra (front panel) of the intermediate acetamide, and the final product, acetic acid, in water under ambient conditions are shown.

Deuteration

Hydrogen atom exchange of a range of aromatic compounds in neutral near-critical D_2O has been improved by using a polymer-supported sulfonic acid catalyst such as Deloxan[®] [24]. Phenol, aniline, quinoline, and substituted aromatic hydrocarbons were selectively ring-perdeuterated in high yields with almost no by-product formation at $325\text{ }^\circ\text{C}$ for 24 h in $\text{D}_2\text{O}/\text{Deloxan}$ (Table 7). In most of the cases, D-incorporations $>90\%$ were achieved.

This reaction performed in a high T/p batch reactor could be suitable for the preparation of deuterated aromatic substrates on a preparative scale.

Table 7 H-D exchange of aromatic compounds in D₂O/Deloxan at 325 °C for 24 h^a [24].

Substrate	Product ^{c,d,e}	% H-D exchange ^f
Phenol	Phenol-d ₇	90
Phenol (no cat.) ^b	Phenol-d ₃	<i>o,p</i> : 89; <i>m</i> : 16
Aniline	Aniline-d ₇	81
Aniline (250 °C, 2 h, no cat.)	Aniline-d ₃	<i>o,p</i> : 92; <i>m</i> : 1
Quinoline	Quinoline-d ₇	76
Ethylbenzene	Ethylbenzene-d ₅	<i>ring</i> : 95, <i>Me</i> : 9
Ethylbenzene (no cat.)	Ethylbenzene-d ₅	<i>ring</i> : 22, <i>Me</i> : 1
Naphthalene	Naphthalene-d ₈	91
Anthracene	Anthracene-d ₁₀	94
Phenanthrene	Phenanthrene-d ₁₀	95
Pyrene	Pyrene-d ₁₀	94
Fluorene	Fluorene-d ₁₀	92
Acenaphthene	Acenaphthene-d ₁₀	86
4-Toluic acid	4-Toluic acid-d ₄	<i>ring</i> : 58, <i>Me</i> : 8
Acetophenone	Acetophenone-d ₃	<i>ring</i> : 10, <i>Me</i> : 90

^aReactions performed in a high T/p autoclave reactor.

^bSimilar results were achieved at 250 °C in: (i) D₂O/Deloxan for 24 h or (ii) D₂O for 2 h.

^cYields >90 %.

^dGC purity >90 %.

^eProduct recovery >90 %.

^fDetermined by mass spectrometry.

CONCLUSION

The unique properties of HTW can be successfully used to carry out various organic transformations reproducibly, selectively, and in high yield. The reactions presented here show that HTW can play the roles of the reactant, the catalyst, or the solvent, or of all three, which makes the HTW process very efficient. Experiments have been carried out both in mini-autoclaves and continuous-flow reactors, which have allowed us to study the reactivity of a wide range of compounds with different functional groups and catalytic requirements. Online spectroscopy (UV–vis and Raman) has allowed us to monitor the chemistry as it happens and change the reaction conditions accordingly to maximize the yield and selectivity.

Our current research is focusing on scalable processes and selective reactions yielding value-added products using particularly continuous-flow systems and water as an environmentally benign alternative to volatile organic solvents.

ACKNOWLEDGMENTS

The work described here includes contributions from Drs. P. A. Hamley, L. M. Dudd, E. Venardou, E. Garcia-Verdugo, C. Boix, J. Garcia-Serna, and Prof. Y. E. Gorbaty. We thank The Royal Society for supporting the collaboration with Russia to develop the high-temperature and -pressure UV–vis, IR, and Raman cells and the School of Chemistry Workshop for reactor development. We are grateful to The Royal Society, GlaxoSmithKline, INVISTA™, The Marie Curie Programme, and the EPSRC for funding.

REFERENCES

1. (a) M. Poliakoff, P. Anastas. *Nature* **413**, 257 (2001); (b) M. Poliakoff, J. M. Fitzpatrick, T. R. Farren, P. Anastas. *Science* **297**, 807 (2002).
2. (a) H. Weingärtner, E. U. Franck. *Angew. Chem., Int. Ed.* **44**, 2672 (2005); (b) E. Dinjus, A. Kruse. *J. Phys.: Condens. Matt.* **16**, 1161 (2004); (c) N. Akiya, P. E. Savage. *Chem. Rev.* **102**, 2725 (2002); (d) R. W. Shaw, B. B. Brill, A. A. Clifford, C. A. Eckert, E. U. Franck. *Chem. Eng. News* **69**, 26 (1991).
3. (a) E. Lester, P. Blood, J. Denyer, D. Giddings, B. Azzopardi, M. Poliakoff. *J. Supercrit. Fluids* **37**, 209 (2006); (b) A. Cabañas, M. Poliakoff. *J. Mater. Chem.* **11**, 1408 (2001); (c) A. Cabañas, J. A. Darr, E. Lester, M. Poliakoff. *J. Mater. Chem.* **11**, 561 (2001); (d) A. A. Galkin, B. G. Kostyuk, V. V. Lunin, M. Poliakoff. *Angew. Chem., Int. Ed.* **39**, 2738 (2000); (e) A. Cabañas, J. A. Darr, M. Poliakoff, E. Lester. *Chem. Commun.* **11**, 901 (2000); (f) T. Adschiri, S. Takami, M. Umetsu, S. Ohara, T. Tsukada. *Ceram. Trans.* **146**, 3 (2005); (g) B. L. Cushing, V. L. Kolesnichenko, C. J. O'Connor. *Chem. Rev.* **104**, 3893 (2004); (h) Y. Hakuta, T. Ohashi, H. Hayashi, K. Arai. *J. Mater. Res.* **19**, 2230 (2004); (i) K. J. Ziegler, R. C. Doty, K. P. Johnston, B. A. Korgel. *J. Am. Chem. Soc.* **123**, 7797 (2001); (j) T. Adschiri, Y. Hakuta, K. Sue, K. Arai. *J. Nanoparticle Res.* **3**, 227 (2001); (k) T. Adschiri, Y. Hakuta, K. Arai. *Ind. Eng. Chem. Res.* **39**, 4901 (2000).
4. (a) P. E. Savage. *Chem. Rev.* **99**, 603 (1999); (b) D. Bröll, C. Kaul, A. Krämer, P. Krammer, T. Richter, M. Jung, H. Vogel, P. Zehner. *Angew. Chem., Int. Ed.* **38**, 2998 (1999); (c) E. J. Parsons. *CHEMTECH* **26**, 30 (1996).
5. (a) Z. Y. Ding, M. A. Frisch, L. Li, E. F. Gloyna. *Ind. Eng. Chem. Res.* **35**, 3257 (1996); (b) P. E. Savage. *Catal. Today* **62**, 167 (1998).
6. S. Yesodharan. *Curr. Sci.* **82**, 1112 (2002).
7. Y. Calzavara, C. Jousset-Dubien, G. Boissonet, S. Sarrade. *Energy Conv. Manage.* **46**, 415 (2005).
8. (a) P. A. Hamley, T. Ilkenhans, J. M. Webster, E. Garcia-Verdugo, E. Venardou, M. J. Clarke, R. Auerbach, W. B. Thomas, K. Whiston, M. Poliakoff. *Green Chem.* **4**, 235 (2002); (b) J. B. Dunn, P. Savage. *Environ. Sci. Technol.* **39**, 5427 (2005).
9. E. Garcia-Verdugo, E. Venardou, W. B. Thomas, K. Whiston, W. Partenheimer, P. A. Hamley, M. Poliakoff. *Adv. Synth. Catal.* **346**, 307 (2004).
10. E. Garcia-Verdugo, J. Fraga-Dubreuil, P. A. Hamley, W. B. Thomas, K. Whiston, M. Poliakoff. *Green Chem.* **7**, 294 (2005).
11. F. M. Lee, W. Lamshing, R. W. Wytsherley, R. Wright. U.S. Patent 6,054,610, HFM International, Inc. (1998).
12. Y. Chen, J. L. Fulton, W. Partenheimer. *J. Am. Chem. Soc.* **127**, 14086 (2005).
13. J. B. Dunn, P. E. Savage. *Green Chem.* **5**, 649 (2003).
14. J. Fraga-Dubreuil, J. Garcia-Serna, E. Garcia-Verdugo, L. M. Dudd, G. R. Aird, W. B. Thomas, M. Poliakoff. *J. Supercrit. Fluids* (2006). In press.
15. (a) <http://www.caruschem.com/air_purification.htm>; (b) A. Martin, U. Armbruster, M. Schneider, J. Radnik, M. Pohl. *J. Mater. Chem.* **12**, 639 (2002).
16. C. Boix, M. Poliakoff. *J. Chem. Soc., Perkin Trans. 1* **11**, 1487 (1999).
17. C. Boix, J. Martinez de la Fuente, M. Poliakoff. *New J. Chem.* **23**, 641 (1999).
18. E. Garcia-Verdugo, Z. Liu, E. Ramirez, J. Garcia-Serna, J. Fraga-Dubreuil, J. R. Hyde, P. A. Hamley, M. Poliakoff. *Green Chem.* **8**, 359 (2006).
19. L. M. Dudd, E. Venardou, E. Garcia-Verdugo, P. Licence, A. J. Blake, C. Wilson, M. Poliakoff. *Green Chem.* **5**, 187 (2003).
20. P. A. Aleman, C. Boix, M. Poliakoff. *Green Chem.* **1**, 65 (1999).
21. A. Kramer, S. Mittelstadt, H. Vogel. *Chem. Eng. Technol.* **21**, 494 (1998).

22. E. Venardou, E. Garcia-Verdugo, S. J. Barlow, Y. E. Gorbaty, M. Poliakoff. *Vib. Spectrosc.* **35**, 103 (2004).
23. (a) Y. E. Gorbaty, G. V. Bondarenko, E. Venardou, S. J. Barlow, E. Garcia-Verdugo, M. Poliakoff. *Vib. Spectrosc.* **35**, 97 (2004); (b) Y. E. Gorbaty, G. V. Bondarenko, E. Venardou, E. Garcia-Verdugo, M. Sokolova, J. Ke, M. Poliakoff. *Appl. Spectrosc.* **57**, 1300 (2003); (c) Y. E. Gorbaty, E. Venardou, E. Garcia-Verdugo, M. Poliakoff. *Rev. Sci. Instrum.* **74**, 3073 (2003).
24. C. Boix, M. Poliakoff. *Tetrahedron Lett.* **40**, 4433 (1999).