Contents lists available at SciVerse ScienceDirect



The Journal of Supercritical Fluids



journal homepage: www.elsevier.com/locate/supflu

Hydration of terminal alkynes on Nafion film in supercritical carbon dioxide

Ol'ga A. Kizas*, Dmitrii Yu. Antonov, Yuri E. Vopilov, Ivan A. Godovikov, Alexander S. Peregudov, Nikolay D. Kagramanov, Ludmila N. Bulatnikova, Lev N. Nikitin, Alexei R. Khokhlov

A.N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, Vavilova 28, 119991, Moscow, Russia

ARTICLE INFO

Article history: Received 19 December 2012 Received in revised form 31 January 2013 Accepted 1 February 2013

Keywords: Supercritical carbon dioxide Nafion film Alkynes hydration Carbenium ion isomerization

ABSTRACT

To find out the conditions for mild hydration of carbon–carbon triple bonds the hydration reactions of some terminal alkynes (FcC=CH, PhC=CH, $C_5H_{11}C=CH$) on the Nafion film in supercritical carbon dioxide (sc-CO₂) were studied. The corresponding ketones were prepared in excellent yields. The hydration of 1-heptyne is accompanied by the isomerization of the terminal carbon–carbon triple bond into the internal one under acidic heterogeneous catalysis.

© 2013 Elsevier B.V. All rights reserved.

1. Introduction

The hydration of alkynes, generating different carbonyl derivatives and connecting two important classes of organic compounds is known since 1860. This reaction is exergonic, thus it is enormously promising in organic synthesis and provides the selective transformations under mild conditions [1–10]. That is why the interest of researchers to this reaction is still very high and a lot of efforts are primarily directed to the search of nontoxic catalysts able to work under mild conditions and easily separable from the reaction products. The heterogeneous catalysts satisfy both of these terms; for instance, a high conversion of ethynylbenzene and a moderate conversion of 1-octyn in hydration reactions were found at 100 °C in 24 h with graphene oxide as a catalyst [11].

So, a search for heterogeneous catalysts for the "green" hydration of carbon-carbon triple bond at moderate temperatures is urgent. The mild hydration reactions may be very useful in the synthesis of complex molecules which are labile at elevated temperatures. A compatibility of the environment-friendly supercritical carbon dioxide with the obvious advantages of the heterogeneous catalyst of the polymeric nature, which can be easily separated from the reaction products, provides the process with the "green" features.

In the present work we succeeded to carry out the alkyne hydration in noticeably milder conditions, keeping the high conversion of the starting alkynes. The fluorinated sulfopolymer Nafion [12]—the superacidic [13–15] heterogeneous catalyst,

which is simultaneously a source of both protons and water, was chosen as a catalyst for the hydration procedure. Nafion contains the ionic channels formed due to the phase division between the hydrophobic polymeric chain and the hydrophilic acidic sulfogroups. The protons transfer proceeds in these channels, which contain water molecules that either are bound with sulfo-groups or fill the space of the channels [16,17]. In our case the water content in the Nafion film of 5% wt was determined according to Fischer just prior to use. Supercritical carbon dioxide (sc-CO₂) was chosen as a solvent having a series of advantages [18-23] comparing with the other ones, *i.e.* the absence of gas-liquid mass transfer limitations, relatively high rates of molecular diffusion and heat transfer, and the possibility of molecular interactions with the dissolved reacting species (substrates or catalysts) [24-31]. An additional stimulus for the choice of sc-CO₂ is a possibility to regulate the delivery of alkyne into the channels by varying the pressure in the reactor. This can result in interesting effects of enhancing the reaction rates and modifying the product selectivity.

2. Experimental

2.1. General

In this work Nafion[®]112 film (thickness 0.002 in.) was purchased from Aldrich, was used as a catalyst for the hydration reaction of alkynes. The 5% water content was not taken into account on calculation of equivalent proton content in Nafion film. The Ethynylferrocene **1** was prepared by known method [32]. Ethynylbenzene **2** (98% purity) and 1-heptyne **3** (98% purity) were purchased from Adrich. N,N-Dimethylformamide was distilled from P_2O_5 at reduced pressure (2 mm Hg), dimethyl sulfoxide

^{*} Corresponding author. Tel.: +7 499 1351017; fax: +7 499 1355085. *E-mail address:* kizas@ineos.ac.ru (O.A. Kizas).

^{0896-8446/\$ -} see front matter © 2013 Elsevier B.V. All rights reserved. http://dx.doi.org/10.1016/j.supflu.2013.02.001

was distilled from CaH₂ at reduced pressure (2 mm Hg). CDCl₃ (D, 99.8%) was purchased from Cambridge Isotope Laboratories, Inc. High purity CO₂ (>99.997%, 0.001% H₂O) was used as received. The pressure generator (High Pressure Equipment, USA) was used and the pressure in the cell was maintained with an accuracy of at least ± 0.2 MPa. All experiments were carried out in the stainless steel 10 cm³ cell. NMR spectra were registered on a Bruker Avance-600 spectrometer at 600.22 MHz for ¹H and 150.92 MHz for ¹³C in CDCl₃ (relative to Me₄Si). GLC-MS analysis: the samples of mixtures were pinned up in an GLC injector Varian 3400, of the chromatograph attached to mass spectrometer VG Analytitsal 7070E. The separation of reaction products were made on a capillary column RTX-5ms (type phase: 5% Phenyl Polysilphenylene-siloxane); the internal diameter of 0.25 mm; the thickness of a film of a phase 0.25 µm; the length 30 m. The injector temperature 250 °C; the dumping 1:50; the initial temperature of the column 34°C, the isotherm 4 min; heating 10°C/min up to 200°C.

2.1.1. Preparation of acetylferrocene (4)

Ethynylferrocene **1** (0.02 g, 0.1 mmol) and Nafion film 0.06 g (eq. wt. 1.100; 0.05 eq. H⁺) were placed in the reaction cell. The cell was heated up to 33 °C and the pressure of CO₂ 20 MPa was created. The reaction mixture was maintained at 33 °C for 3 h, then by means of the gate of thin adjustment, the pressure of CO₂ was dumped within 10–15 min. The Nafion film having deep garnet color was washed with acetone or chloroform. The solution instantly became redorange and the film gained natural color (reuse of the film leads to the same result). The solvent was evaporated at reduced pressure, and the residue analyzed in CDCl₃ solution by NMR ¹H and ¹³C. The red-orange crystals were washed out from the walls of the reaction cell. The solvent was evaporated at reduced pressure, and the residue showed the presence of **4** as the sole product [33].

2.1.2. Preparation of acetophenone (5)

Ethynylbenzene **2** (0.2 mL, 1.8 mmol) and Nafion film 0.5 g (eq. wt. 1100; 0.45 eq. H⁺), or **2** (0.2 mL, 1.8 mmol) and Nafion film 1.0 g (eq. wt. 1100; 0.9 eq. H⁺) were placed into reaction cell and was heated to the necessary temperature. The reaction conditions are presented in Table 1. The pressure of CO_2 was dumped during 3–4 h. Then the reaction cell with the Nafion film was washed with raw acetone (4 × 10 mL) and the solution was allowed to stand for 15–20 min. The solvent was removed, and the residue was analyzed by NMR. In the case of considerable dimness of the film at repeated use of the catalyst it is necessary for its regeneration to maintain the film in ethanol during 10–12 h.

2.1.3. Preparation of 2-heptanone (**6**)

1-Heptyne **3** (0.2 mL, 1.8 mmol) and Nafion film 1.0 g (eq. wt. 1100; 0.9 eq. H^+) were heated in sc CO₂ under conditions presented

Table 2

The transformation of 1-heptyne $\mathbf{3}$ on Nafion film^a in sc-CO₂.

Table 1

Hydration^a of ethynylbenzene **2** on Nafion film in sc-CO₂.^b

Entry	Ratio 2 /Nafion	$T(^{\circ}C)$	Number of cycles	Conversion ^c of 2 %
1	1/0.25	33	1	100
2	1/0.25	33	2	93
3	1/0.25	55	4	100
4	1/0.5	33	4	100
5	1/0.5	55	4	100

^a Reaction time: 12 h. ^b $P CO_2 = 20 MPa$.

^c The conversion was determined from the spectra NMR ¹H in CDCl₃.

R−с≡с−н	Nafion-film	R−C			
	sc-CO ₂	СН₃			
1 R=Fc		4 acetylferrocene			
2 R=Ph		5 acetophenone			
3 R=C ₅ H ₁₁		6 2-heptanone			

Scheme 1. The hydration of the terminal alkynes on Nafion film in sc-CO₂.

in Table 2. The pressure of CO_2 was dumped during 4–6 h. The reaction cell with the Nafion film was washed with 1 mL of $CDCl_3$. The film was exposited within 2–3 h in this solution, which then was analyzed by NMR (Fig. 1)

3. Results and discussion

The hydration of the terminal alkynes R-C=C-H (1-3) [1:Ethynylferrocene (R=Fc), 2: Ethynylbenzene (R=Ph), 3: 1-Heptyne (R=C₅H₁₁)] on Nafion film in sc-CO₂ was carried out under the mild conditions and resulted in the quantitative yields of both acetylferrocene **4** and acetophenone **5** respectively, and high yields of 2-heptanone **6** (Scheme 1).

It is known that the acid-catalyzed hydration of alkynes proceeds *via* a formation of vinyl-cations [34–36]. A set of the alkynes chosen for the study permits to demonstrate an influence of the substituent R in the alkyne on a stability of the intermediate vinyl carbenium ion and on the rate of formation of the hydration product RC(O)CH₃. The hydrations of acetylenes having the substituent able to stabilize the intermediate cation center were carried out under conditions of homogeneous catalysis at moderate temperatures and in relatively high yields: H₂SO₄(aq)/60 °C([1] and references cited therein), H₂SO₄/–20 °C [37], H₂SO₄/–10 °C [38], TFA(aq)/25 °C [39]. The stabilization of carbenium ion goes down in a series ethynylferrocene **1** > ethynylbenzene **2** > 1-heptyn **3** [40,41] causing the increase of the reaction temperature or prolongation of the process duration going from **1** to **3**.

Thus, ethynylferrocene **1** transforms into acetylferrocene **4** at the ratio alkyne/Nafion = 1/0. of CO₂ ($31.1 \degree$ C and 7.5 MPa—the minimum values of temperature and pressure for the living conditions

Entry	Time (h)	T (°C)	P(MPa)	The compo	The composition of the reaction mixture %						Conversion ^b of 3 (%)	
				$C_5H_{11}C = CH$ 3 $C_5H_{11}C = 0)CH_3$ 6		D)CH ₃ 6	C ₄ H ₉ CH=C=CH ₂ 7		$C_3H_7C \equiv CC_2H_5$ 8			
				NMR ¹ H	GLC-MS	NMR ¹ H	GLC-MS	NMR ¹ H	GLC-MS	NMR ¹ H	GLC-MS	
1	10	90	20	54.4	-	32.1	-	4.4	-	9.2	-	45.6
2	12	93	20	48.8	48.5	37.5	35.8	3.9	3.8	10.3	11.8	51.2
3	15	93	20	41.8	-	43.1	-	3.8	-	11.4	-	58.2
4	15	93	35	41.5	-	47.5	-	3.5	-	7.5	-	58.5
5	15	98	20	38.2	-	45.5	-	3.6	-	12.6	-	61.8
6	20	93	20	33.6	32.6	48.7	47.1	3.1	5.9	14.5	14.3	66.4

^a Molar ratio 3/Nafion film = 1/0.5.

^b Conversion was determined from the NMR ¹H spectra in CDCl₃.



Fig. 1. (a) NMR ¹H (600.22 MHz, CDCl₃) and (b) NMR ¹³C (150.92 MHz, CDCl₃) spectra of the reaction mixture transformation 1-heptyn **3** on Nafion film in sc-CO₂ (a) for **6**: δ 2.42 (virtual t, 2H, ³ J_{H-H} = 7.49 Hz, CH₂C(=0)CH₃), 2.14 (s, 3H, (C=0)CH₃); for **7**: 5.12–5.07 (m, 1H, CH=C=), 4.66–4.63 (m, 2H, =C=CH₂), 2.03–1.97 (m, 2H, CH₂CH=C=); for **8**: 2.15–2.1 (m, 2H, =CCH₂CH₃), 1.78 (t, 3H, ³ J_{H-H} = 2.53 Hz, =CCH₂CH₃). (b) for **6**: δ 209.37 (C=O), 18.35 (O=CCH₃); for **7**: 208.49 (=C=) [50], 90.04 (CH=C=), 74.47 (=C=CH₂); for **8**: 79.32, 75.27 (C=C), 18.39 (=CCH₂CH₃), 3.45 (=CCH₂CH₃).

of supercritical CO₂) during 3 h. After the reaction completion the painted compound is completely washed away from a film by CDCl₃. After the reaction completion the painted compound is completely washed away from a film by CDCl₃. The NMR ¹H spectrum of solution shows the signals only of **4** [33]. The convertion of ethynylbenzene **2** also proceeded quantitatively, but longer time was required. The summarized results of experiments are presented in (Table 1). The conversion of ethynylbenzene **2** achieves 100% at 33 °C at the **2**/Nafion ratio = 1/0.25 (Table 1, entry 1), and 93% during the second use of the same catalyst and under similar conditions (Table 1, entry 2). The catalyst activity (the ratio of **2**/Nafion = 1/0.25) remained unchanged after its fourfold use at

55 °C. It is well known that the reactivity of polymers increase on swelling which is proportional to the temperature [42,43]. The increasing the catalyst loading up to 2/Nafion = 1/0.5 ratio leads to the same effect (Table 1, entries 4, 5).

The value 20 MPa of sc-CO₂ pressure is important for successful course of the hydration reaction of terminal alkynes on Nafion film. It is known that both a rise in of sc-CO₂ pressure and higher temperature increase swelling of polymers, with the optimal pressure being as high as 20 Mpa [43,44], which is true for Nafion [45], too. So, we can speculate that this is the case with our study. Really, the increasing of the pressure (Table 2, entries 4) does not effect on the conversion of the 1-heptyne **3**, while its diminishing to 10 MPa



Scheme 2. The isomerization of terminal triply bond into internal one in 1-heptyne.

leads to the reduction of the conversion of ethynylbenzene **2** to 13% in the first catalytic cycle (35 °C; ratio **2**/Nafion = 1:0.25), while 1-heptyne **3** under these conditions was not hydrated at all. We believe that 20 MPa is the pressure at which the acetylenes reach the centers of protonation in the Nafion film most efficiently.

It is very interesting that ethynylbenzene **2** practically cannot be hydrated in the solution of Nafion oligomer in N,N-Dimethylformamide or Dimethyl sulfoxide at 33 or 55 °C during 30 days, while for ethynylferrocene **1** this reaction proceeds. This is probably caused by the various energies of stabilization of the corresponding vinyl cations.

The hydration of 1-heptyne **3** proceeds in a high yields under even more rigid conditions (Table 2). It practically does not occur at the temperature below $85 \,^\circ$ C. We failed to achieve the quantitative conversion for the hydration of **3** that was presumably caused by water loss by the catalyst at the temperature $93 \,^{\circ}$ C. It is known that Nafion losses the water at the temperatures higher than $90 \,^{\circ}$ C and its reimbursement is reached by the special procedures or by modification of the polymer [16]. The rate of the catalyst deactivation should grow up with the increase [46] of alkyn/H₂O ratio as occurs in our case judging by the presence of 1,2-heptadiene **7** and 3-heptyne **8** in the reaction mixture (Table 2), and the reduction of the conversion of 1-heptyne **3** during the second cycle to 30%. Moistening the film or addition of water to the steel cell did not lead to the increase of the starting alkyne conversion.

The irreversible loss of water from Nafion film allowed us to obtain the interesting results concerning the acetylene–allene rearrangement of terminal alkynes. The interaction of 1-heptyne **3**



Fig. 2. NMR HC-HMBC (600.22 MHz, CDCl₃) spectrum for signals --CH=C= and =C=CH₂ groups of 7.

with dehydrated Nafion which is a strong acid leads to the isomerization of this terminal alkyne into the internal one (Scheme 2). It was shown earlier that terminal alkynes in the acidic media reversibly convert to allenes which in turn isomerize into dienes, and no isomerization of the terminal triple bond to the internal one was observed [47]. It is well known that the isomerization of the internal triple bond into the terminal one proceeds successfully in alkaline media via allene intermediates [48]. Nevertheless, some literature data indicate that the reverse process, *i.e.* an isomerization of the terminal bond into the internal one via allene intermediates, is possible to carry out under the influence of very strong acids [49]. The transformation of 1-heptyne **3** on Nafion film leads to the formation of the products mixture with the acetophenone 6 as a major component and the 1,2-heptadiene 7 and the 3-heptin **8** as the minor ones. The structure of the reaction products and their yields were established by GLC-MS and NMR spectral data (Table 2). The assignment of signals in NMR spectra was made on the basis of one- and two-dimensional experimental spectral data (Figs. 1a and b, and 2) and the NMR spectra ¹H-¹³C, HMBCGP, COSY (Supplementary Date, Fig. S1-S6).

The presence of 3-heptyne **8** in the reaction mixture testifies that we have found the first example of the isomerization of the terminal triple bond into the internal one under conditions of heterogeneous acidic catalysis. We believe the reaction to proceed as a sequence of the protonation and deprotonation steps as have been described earlier [49] though we did not succeed in detecting both 2-heptyn **9** and 2,3-heptadiene **10**, the precursors of 3-heptyne **8** (Scheme 2), in the reaction mixture. In our opinion, the products composition is defined by the thermodynamic stability of intermediate cations causing the formation of 1,2-heptadiene **7** and and 3-heptin **8**.

4. Conclusions

In this work an effective method for hydration of alkynes including the alkyl substituted one in sc-CO₂ have been elaborated. The hydration proceeds in the presence of Nafion film as the catalyst that gives rise the excellent results (100% conversion at low temperature (33 or 55 °C without decrease of activity of the catalyst during several repeated reaction cycles) in the case of alkynes bearing substituents capable to stabilize the arising cationic center. The merits of the catalytic system along with simplicity of the isolation of the products make this reaction a promising method for the hydration of both functionalized and hetaryl substituted alkynes. In addition, the terminal carbon–carbon triple bond in 1-heptyne was shown to migrate into the internal position under the acid heterogeneous catalysis conditions.

Acknowledgments

This work was financially supported by the RFBR (Grant No. 11-03-91169-GFEN).

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.supflu. 2013.02.001.

References

- L. Hintermann, A. Labonne, Catalytic hydration of alkynes and its application in synthesis, Synthesis (2007) 1121–1150.
- [2] H. Stetter, Ketone durch Hydratisierung von Alkinen and Allenen, in: E. Müller (Ed.), Methoden der Organischen Chemie (Houben-Weyl), vol. VII/2a, 4th ed., Georg Thieme, Stuttgart, 1973, pp. 816–842.
- [3] B. Figadere, X. Franch, Synthesis by Addition, in: J. Cossy, J Cossy (Eds.), Science of synthesis, vol. 26, Georg Thieme, Stuttgart, 2005, pp. 401–411.

- [4] S.V. Ley, J. Norman, W.P. Griffith, S.P. Marsden, Tetrapropylammonium perruthenate, Pr4N+ RuO4–, TPAP. A catalytic oxidant for organic synthesis, Synthesis (1994) 639–666.
- [5] K. Tani, Y. Kataoka, O.-H. Activation, Addition to unsaturated systems, in: A. Togni, H. Grützmacher (Eds.), Catalytic heterofunctionalization, Wiley-VCH, Weinheim, 2001, pp. 171–216.
- [6] F. Chevaller, B. Breit, Self-assembled bidentate ligands for Ru-catalyzed antimarkovnikov hydration of terminal alkynes, Angewandte Chemie International Edition (2006) 1599–1602.
- [7] T. Kribber, A. Labonne, L. Hintermann, Iterative synthesis of oligo-1,4-diols via catalytic anti-markovnikov hydration of terminal alkynes, Synthesis (2007) 2809–2818.
- [8] D.-M. Cui, Y.-N. Ke, D.-W. Zhuang, Q. Wang, C. Zhang, A. Togni, Gold-catalyzed hydrative cyclization of 1,6-diynes in ionic liquid media, Tetrahedron Letters (2010) 980–982.
- [9] M. Lein, M. Rudolph, S.K. Hashmi, P. Schwerdtfeger, Homogeneous gold catalysis: mechanism and relativistic effects of the addition of water to propyne, Organometallics 29 (2010) 2206-2210.
- [10] A. Leyva-Perez, A. Corma, Similarities and differences between the relativistic triad gold, platinum, and mercury in catalysis, Angewandte Chemie International Edition (2012) 614–635.
- [11] D.R. Dreyer, H.-P. Jia, C.W. Bielawski, Graphene Oxide, A Convenient carbocatalyst for facilitating oxidation and hydration reactions, Angewandte Chemie International Edition (2010) 6813–6816.
- [12] US Patent 003,041,317, 1962.
- [13] J.A. Elliott, S. Hanna, A.M.S. Elliott, G.E. Cooley, The swelling behaviour of perfluorinated ionomer membranes in ethanol/water mixtures, Polymer 42 (2001) 2251–2253.
- [14] G. Gelbard, Organic synthesis by catalysis with ion-exchange resins, Industrial & Engineering Chemistry Research 44 (2005) 8468–8498.
- [15] V.I. Šokolov, L.N. Nikitin, L.A. Bulygina, V.N. Khrustalev, Z.A. Starikova, A.R. Khokhlov, Supercritical carbon dioxide in organometallic synthesis: Combination of sc-CO₂ with Nafion film as a novel reagent in the synthesis of ethers from hydroxymethylmetallocenes, J. Organometallic Chemistry (2010) 799–803.
- [16] S.S. Ivanchev, S.V. Myakin, Polymer membranes for fuel cells: manufacture, structure, modification, properties, RUSS Chemical Reviews 79(2010) 101–117.
- [17] K.-D. Kreure, Hydrocarbon membranes, in: W. Vielstich, A. Lamm, H.A. Gasteiger (Eds.), Handbook of fuel cells: fundamentals, technology and applications, vol. 3, full cell technology and applications, Pt. 1, John Wiley & Sons Ltd., Chichester, 2003, pp. 420–435.
- [18] A. Baiker, Supercritical fluids in heterogeneous catalysis, Chemical Reviews 99 (1999) 453–474.
- [19] P.G. Jessop, T. Ikariya, R. Noyori, Homogeneous catalysis in supercritical fluids, Chemical Reviews 99 (1999) 475–494.
- [20] A. Darr, M. Poliakoff, New directions in inorganic and metal-organic coordination chemistry in supercritical fluids, Chemical Reviews 99 (1999) 495–542.
- [21] E.J. Beckmann, Supercritical and near-critical CO₂ in green chemical synthesis and processing, J. Supercritical Fluids 28 (2004) 121–191.
- [22] P.G. Jessop, Homogeneous catalysis using supercritical fluids: recent trends and systems studied, J. Supercritical Fluids 38 (2006) 211–231.
- [23] C.M. Rayner, The potential of carbon dioxide in synthetic organic chemistry, Organic Process and Research Development 11 (2007) 121–132.
- [24] S. Fujita, H. Yoshida, K. Asai, X. Meng, M. Arai, Selective hydrogenation of nitrostyrene to aminostyrene over Pt/TiO₂ catalysts: effects of pressurized carbon dioxide and catalyst preparation conditions, J. Supercritical Fluids 60 (2011) 106–112.
- [25] M.O. Gallyamov, I.S. Chaschin, A.I. Camzazade, A.R. Khokhlov, Chitosan molecules deposited from supercritical carbon dioxide on a substrate: visualization and conformational analysis, Macromolecular Chemistry and Physics 209 (2008) 2204–2212.
- [26] D.K. Morita, D.R. Pesiri, S.A. David, W.H. Glase, W. Tumas, Palladium-catalyzed cross-coupling reactions in supercritical carbon dioxide, Chemical Communications (1998) 1397–1398.
- [27] R.S. Gordon, A.B. Holmes, Palladium-mediated cross-coupling reactions with supported reagents in supercritical carbon dioxide, Chemical Communications (2002) 640–641.
- [28] S.E. Lybimov, I.V. Kuchurov, T.A. Verbitskaya, E.A. Rastorgueva, V.N. Kalinin, S.G. Zlotin, V.A. Davankov, Pd-catalyzed allylic amination in supercritical carbon dioxide: Synthesis of carborane-containing terpenoids, J. Supercritical Fluids 54 (2010) 218–221.
- [29] A. Galia, O. Scialdone, E. Tortorici, Transesterification of rapeseed oil over acid resins promoted by supercritical carbon dioxide, J. Supercritical Fluids 56 (2011) 186–193.
- [30] L.-I. Rodriguez, O. Rossell, M. Seco, A. Orejyn, A.M. Masdeu-Bulty, Palladocarbosilane dendrons in supercritical carbon dioxide. Catalytic behaviour in the asymmetric hydrovinylation of styrene, J. Supercritical Fluids 55 (2011) 1023–1026.
- [31] E.M.A. Guerrero-Gutierres, D. Suleiman, Supercritical fluid CO₂ processing and counter ion substitution of nafion[®] membranes, J. Applied Polymer Science (2012) 1–13.
- [32] M. Rosenblum, N. Brawn, J. Parenmeier, M. Applebaum, Synthesis of ferrocenylacetylenes, J. Organic Chemistry 6 (1966) 173–180.
- [33] L.R. Kenneth, A.P. Sloan, D.E. Bublitz, D.H. Gustafson, Organic chemistry of ferrocene. VI. Acetylation of mono-, di- and tri-bridged ferrocenes, J. American Ceramic Society (1963) 970–982.

- [34] Y. Chiang, A.J. Kresge, M. Capponi, J. Wirz, Direct observation of acetophenone enol formed by photohydration of phenylacetylene, Helvetica Chimica Acta 69 (1986) 1331–1332.
- [35] P. Wan, S. Culshaw, K. Yates, Photohydration of aromatic alkenes and alkynes, J. American Ceramic Society 104 (1982) 2509–2515.
- [36] T. Wooldridge, T.D. Roberts, Vinyl cations as intermediates in photohydration of acetylenes, Tetrahedron Letters 41 (1973) 4007–4008.
- [37] F. Bohlmann, H.-G. Viehe, Polyacetylenverbindungen, IX. Mitteil, Alkalische und saure Addition an Polyine, Chemische Berichte 88 (1955) 1017–1027.
- [38] P. Ruggli, A. Staub, Über m-Phenylen-di-propiolsäure und m-Di-acetyl-benzol (25. Mitteilung über Stickstoff-Heterocyclen), Helvetica Chimica Acta 19 (1936) 962–972.
- [39] B. Meseguer, D. Alonso-Diaz, N. Griebenow, T. Herget, H. Waldmann, Natural product synthesis on polymeric supports—synthesis and biological evaluation of an indolactam library, Angewandte Chemie International Edition 38 (1999) 2902–2906.
- [40] A.N. Nesmeyanov, K.I. Granberg, N.A. Zharikova, S.P. Gubin, Electronic influence of ferrocenyl as a substituent, Izvestiya Academii Nauk USSR, Seriya Chimicheskaya 5 (1966) 832–839, Chemical Abstract 65:5344e.
- [41] K.V. Kilway, A. Streitwieser, Ion-pair acidity of some substituted ferrocenes in tetrahydrofuran. Stabilization of a carbanion by ferrocene, J. Organic Chemistry 64 (1999) 5315–5317.
- [42] C. Cravo, A-R.C. Duarte, C.M.M. Duarte, Solubility of carbon dioxide in a natural biodegradable polymer: determination of diffusion coefficients, J. Supercritical Fluids 40 (2007) 194–199.

- [43] S.E. Bozbag, C. Erkey, Supercritical fluids in fuel cell research and development, J. Supercritical Fluids 62 (2012) 1–31.
- [44] L. Su, S. Pei, H. Li, Y. Zhang, W. Yu, C. Zhou, Preparation of polysiloxane/perfluorosulfonic acid nanocomposite membranes in supercritical carbon dioxide system for direct methanol fuel cell, International Journal of Hydrogen Energy 34 (2009) 6892–6901.
- [45] D. Kim, J. Sauk, J. Byun, K.S. Lee, H. Kim, Palladium composite membranes using supercritical CO₂ impregnation method for direct methanol fuel cells, Solid State Ionics 178 (2007) 865–870.
- [46] G. Gut, K. Aufdereggen, Reaktionskinetische Untersuchungen der Hydratisierung von Acetylen zu Acetaldehyd an Molekularsieben, die mit katalytisch wirksamen Metall-Ionen beladen sind, Helvetica Chimica Acta 57 (1974) 441–452.
- [47] Ya. M. Slobodin, The Izomerization of allenes on silicates, Zhurnal Obshchei Khimii 7 (1937) 2376–2380 [Chemisches Zentralblatt 2 (1938) 1559–1560].
- [48] M. Smith, J. March, Advanced organic chemistry, vol. 2, 5th ed., Wiley & Sons, New York/Chichester/Weinheim/Brisbane/Singapore/Toronto, 2001, p. 770–1 [Chapter 12].
- [49] B.J. Barri, W.J. Beale, M.D. Carr, S.-K. Hei, I. Reid, Vinyl cations in acid-catalysed isomerisations of acetylenes and allenes, J. Chemical Society, Chemical Communications (1973) 177.
- [50] E. Pretsch, P. Büllmann, C. Affolter, Structure determination of organic compounds, Springer-Verlag, Berlin, Heideberg, 2000, p. 80–4.