



Hydration of terminal alkynes on Nafion film in supercritical carbon dioxide

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ABSTRACT

To find out the conditions for mild hydration of carbon–carbon triple bonds the hydration reactions of some terminal alkynes ($\text{Fc}\equiv\text{CH}$, $\text{PhC}\equiv\text{CH}$, $\text{C}_5\text{H}_{11}\text{C}\equiv\text{CH}$) on the Nafion film in supercritical carbon dioxide (sc-CO_2) 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.

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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 sulfo-groups. 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-CO_2) 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-CO_2 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

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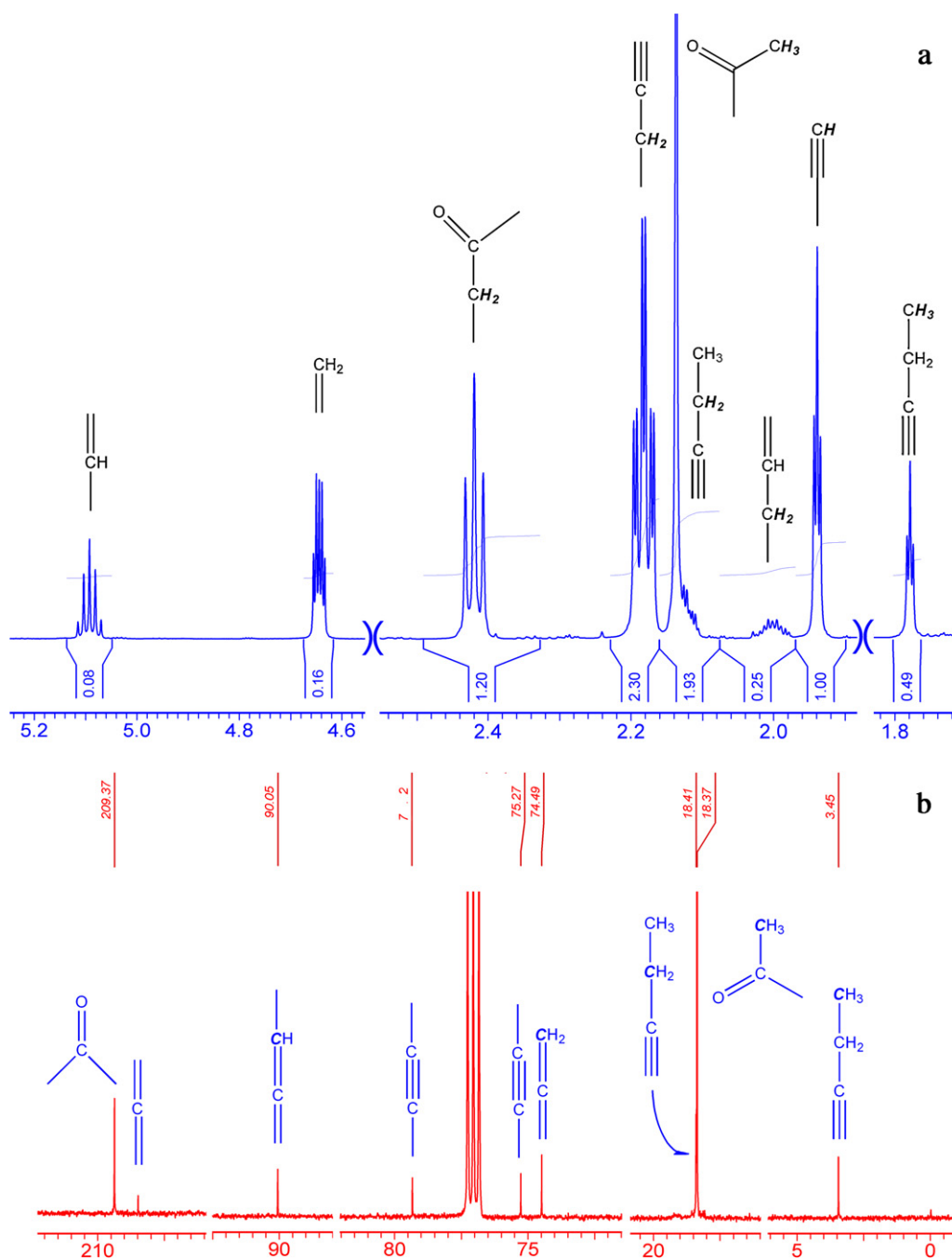
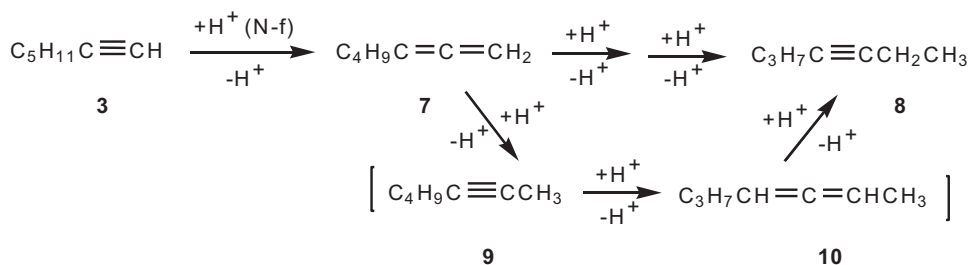


Fig. 1. (a) NMR ^1H (600.22 MHz, CDCl_3) and (b) NMR ^{13}C (150.92 MHz, CDCl_3) spectra of the reaction mixture transformation 1-heptyn **3** on Nafion film in sc-CO_2 (a) for **6**: δ 2.42 (virtual t, 2H, $^3J_{\text{H-H}} = 7.49$ Hz, $\text{CH}_2\text{C}(=\text{O})\text{CH}_3$), 2.14 (s, 3H, $\text{C}(=\text{O})\text{CH}_3$); for **7**: 5.12–5.07 (m, 1H, $\text{CH}=\text{C}=\text{}$), 4.66–4.63 (m, 2H, $=\text{C}=\text{CH}_2$), 2.03–1.97 (m, 2H, $\text{CH}_2\text{CH}=\text{C}=\text{}$); for **8**: 2.15–2.1 (m, 2H, $\equiv\text{CCH}_2\text{CH}_3$), 1.78 (t, 3H, $^3J_{\text{H-H}} = 2.53$ Hz, $\equiv\text{CCH}_2\text{CH}_3$). (b) for **6**: δ 209.37 (C=O), 18.35 (O=CCH₃); for **7**: 208.49 ($\text{C}=\text{C}$) [50], 90.04 ($\text{CH}=\text{C}=\text{}$), 74.47 ($=\text{C}=\text{CH}_2$); for **8**: 79.32, 75.27 (C $\equiv\text{C}$), 18.39 ($\equiv\text{CCH}_2\text{CH}_3$), 3.45 ($\equiv\text{CCH}_2\text{CH}_3$).

of supercritical CO_2) during 3 h. After the reaction completion the painted compound is completely washed away from a film by CDCl_3 . After the reaction completion the painted compound is completely washed away from a film by CDCl_3 . The NMR ^1H spectrum of solution shows the signals only of **4** [33]. The conversion 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-CO_2 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-CO_2 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 °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 °C. It is known that Nafion loses the water at the temperatures higher than 90 °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**

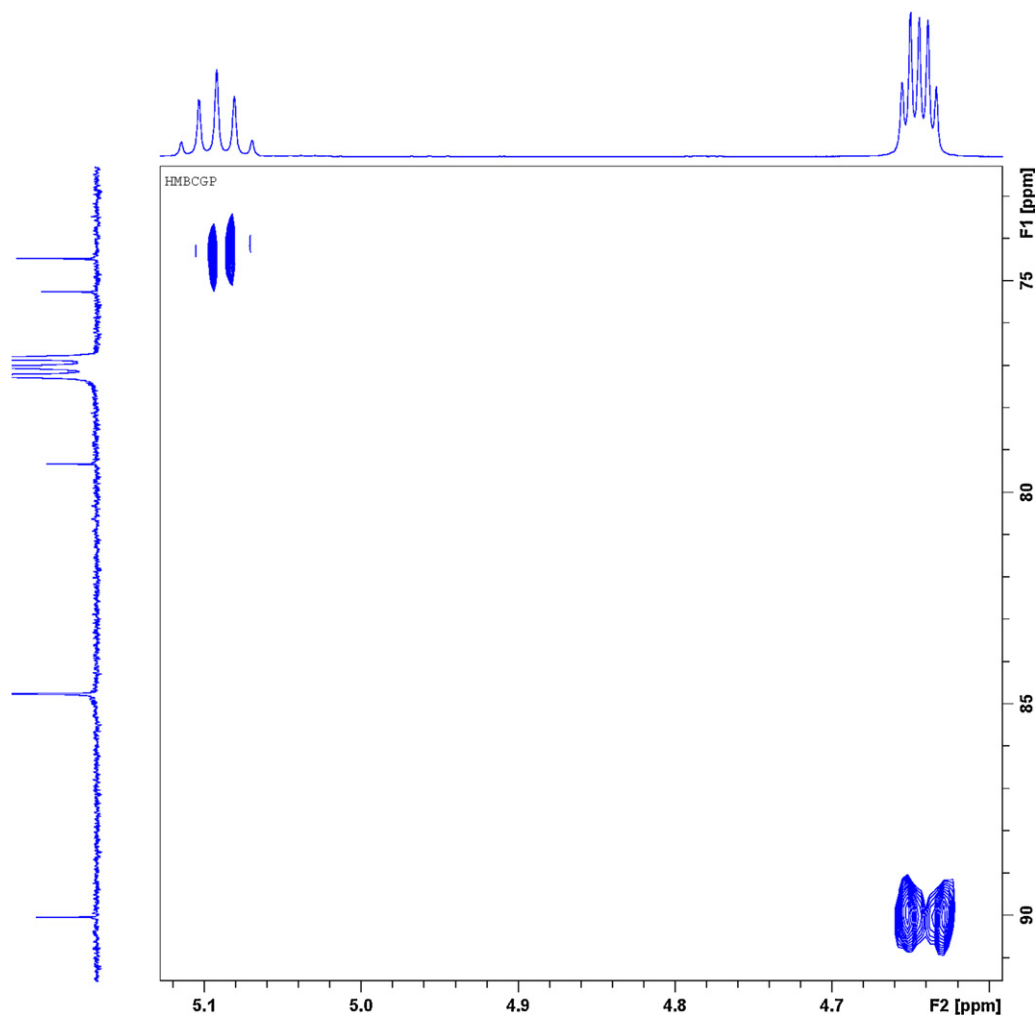


Fig. 2. NMR HC-HMBC (600.22 MHz, CDCl₃) spectrum for signals —CH=C= and =C=CH₂ groups of **7**.

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 – ^{13}C , 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 3-heptin **8**.

4. Conclusions

In this work an effective method for hydration of alkynes including the alkyl substituted one in sc-CO_2 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.

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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>.

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