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INFLUENCE OF MAGNETIC FIELD ON THE REDUCTION OF 4,8-DIAZA-3,6,6,9-TETRAMETHYL UNDECANE-3,8-DIENE-**2,10-DIONE DIOXIME**

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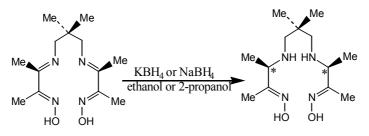
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Abstract

The influence of the magnetic field with the magnetic induction up to 1,35T on the reduction of 4,8-diaza-3,6,6,9-tetramethylundecane-3,8-diene-2,10-dione dioxime (DI) in anhydrous protic solvents (anhydrous ethanol and 2-propanol) was defined. As the reductants NaBH₄ and KBH₄ were used.

Introduction

It is well known that magnetic fields affect water solutions and biological systems, as well as that the magnetic treated water influences the processes in it. However, there are no data on the influence of magnetic fields on chemical reactions, especially those in non-aqueous solutions. The reduction of the two imines groups in DI with NaBH₄ (or KBH₄) in protic solvent (anhydrous ethanol or 2-propanol) provides 4,8-diaza-3,6,6,9-tetramethylundecane-2,10-dione dioxime (HM-PAO) as an equal mixture of the meso- and d,l-diastereoisomers. In our previous work CLEC (Chiral Ligand Exchange Chromatography) method for resolution of the isomers of HM-PAO is described [1]. So, the reaction of reduction can be followed via the quantities of the starting substance and final products.



Results and Discussion

Instrumentation: The analyses were carried out on the Hewlett-Packard HPLC system Model HP 1050 with HP 1100 UV-Visible variable wavelength detector. The separations were performed on the analytical column LiChroCart Superspher 100-RP-18 (125mm x 4mm ID), particle size 5µm (Merck). The magnetic fields were produced by the electromagnets on the Faculty of Physical Chemistry [2] and in the Vinča Institute, providing the magnetic induction up to 1.5 and 1.4 T, respectively.

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Chemicals: The substance 4,8-diaza-3,6,6,9-tetramethylundecane-3,8-diene-2,10dione dioxime was synthesized and characterized according to the method of Canning and Nowotnik [3]. The chiral selector N,N-dimethyl-*l*-phenylalanine (*l*-DM-PhA) 99% (Aldrich) and p.a. grade chemicals (Merck) were used.

Procedure: The mobile phase contained 0.7 mM Cu(II) and 2.8 mM *l*-DM-PhA in pH range 4.1–4.2 (adjusted by acetic acid) and up to 0.8 mM triethylamine. The presaturation procedure for an analytical column (RP-18) and the mobile phase preparation were reported previously [1]. The injection volume was 5 $\mu\ell$, UV detector was set at 225 nm, the flow rate of the eluent was 0.5 m ℓ min⁻¹ and the column temperature was 30°C. Aliquots (50 $\mu\ell$) of the reaction mixtures were diluted with 1 m ℓ of the mobile phase and analyzed. The experiments were performed at room temperature. The reaction mixtures were exposed to the magnetic fields (1-24 h) and analyzed on the same day. The elution order of DI and HM-PAO isomers was previously determined [1]. The reduction reactions were followed with (Analyze) and without (Blank) magnetic field.

Results: The reduction of 0.0227g DI with 0.0035g NaBH₄ (**1**) is presented on the Figs 1 and 2, while the reduction of 0.0227g DI with 0.0045g KBH₄ (**2**) is presented on the Figs 3 and 4, both in $2m\ell$ of anhydrous ethanol. The samples for reduction **1** and **2** were taken after 30 minutes and 3.5 hours, respectively.

Elution order of DI and HM-PAO isomers was previously determined [1], so the peak (1) with retention time t_r =15.4 min belongs to ℓ -isomer, the peak (2) with retention time t_r =16.8 min belongs to *meso*-isomer, the peak (3) with retention time t_r =20.8 min belongs to the starting DI and the peak (4) with retention time t_r =26.5 min belongs to *d*-isomer of HM-PAO.

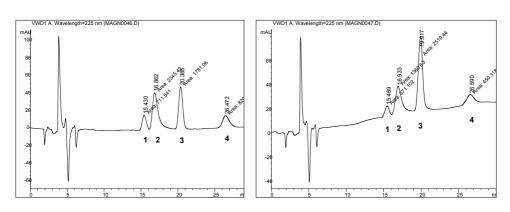
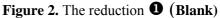


Figure 1. The reduction **1** (Analyze)



The samples of the reductions ① and ② were exposed to the magnetic fields with magnetic induction of the 1.35 T.

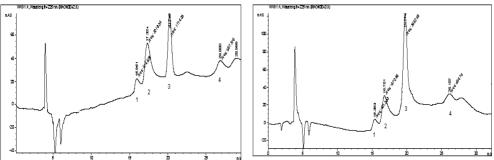


Figure 3. The reduction **2** (Analyze) Figure 4. The reduction **2** (Blank)

As it can be seen in the chromatograms in the reduction **①** the content of the starting DI (peak 3) is much lower in the **Analyze** than in the **Blank** samples, while the content of the final product, HM-PAO isomers, is higher. This indicates that the reduction in the magnetic field is faster. Similar effect is obtained in the reduction **②**, but after a longer period of time. So, it can be concluded that the reduction **③** is significantly faster than the reduction **②**. In the samples taken after 3.5 h, the content of *meso*-isomer of HM-PAO in the Analyze samples is higher (for 3.2-3.5 %, mean value of three experiments), which indicates also the effect of the magnetic field at HM-PAO isomers content. It should be mentioned that the effect of the magnetic field disappeared if the samples were left in the mobile phase for more than 24 h. The contents of the HM-PAO in the Analyze and the Blank samples are the same.

Conclusion

The influence of the magnetic field is observed in the both investigated reduction reactions. The reduction reactions in the magnetic fields are found to be faster. There some indications that the magnetic field influences also the content of the HM-PAO isomers in the reaction mixture. According to the present experience, the effect of the magnetic field on chemical reactions in non-aqueous environment, could be explained by its influence on the molecules of the substance and solvent, especially if the solvent is included in the reaction process. Further investigations are in progress.

References

- N. Nikolić, D. Veselinović, J.Vučina, H. Lingeman, K. Karljiković-Rajić, J. Pharm. Biomed. Anal., 2003, 32, 1159.
- [2] D. Veselinović, D. Ilić, M. Vukić, Book of Abstracts of the Third Yugoslav Simposium "Chemistry and Environment", Vrnjačka Banja 1998, p. 339.
- [3] R. Neirinckx, L. Canning, I. Piper, D. Nowotnik, R. Pickett, R. Holmes, W. Volkert, A. Foster, P. Weisner, J. Marriott, S. Chaplin, J. Nucl. Med., 1987, 28, 191.

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