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Microwave Assisted Oxidation of some aromatics by Hydrogen Peroxide at Supported Tungsten catalyst

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ABSTRACT

The oxidation of some aromatics with the alkyl side groups by hydrogen peroxide has been presented. As the activator of hydrogen peroxide the tungstoboric acid was chosen. The catalyst was examined in both homogeneous and heterogeneous conditions. The reaction in conventional conditions were compared with the microwave assisted reactions.

KEYWORDS

oxidation, hydrogen peroxide, microwaves, tungsten.

INTRODUCTION

Microwave synthesis of organic compounds attracts nowadays a lot of researches because of the shortening in the reaction time, which is very often followed by the improvement in the yield and selectivity [1]. The advantages of microwaves in synthetic organic chemistry has already been shown in many publication [2]. However, these phenomena are still beyond the clear explanation some hypotheses have already been emphasized using dielectric and conducting mechanism of microwave dielectric heating as well as (in some cases) by interphase polarization [3]. The so called "non-thermal" effects has also been suggested by some scientists [4].

The oxidation reactions are one of the most detailed investigated parts of the modern organic synthesis [5]. However, there is still the growing interest in novel methods which will not suffer from toxic wastes and can be characterized by high yield and selectivity. From a number of available oxidants hydrogen peroxide seems to be very promising in terms of non-toxic side product (i.e. water) and high oxidation potential [6]. In fact, oxidation reaction of many organic compounds by H₂O₂ required metal catalyst [7].

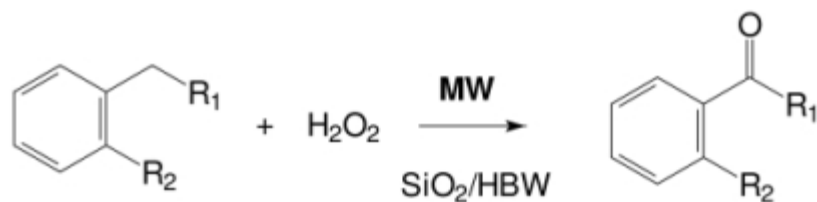
In this context there is still need to investigate the oxidation by H₂O₂ at microwave conditions which is the scope of previous research [8] as well as application of heterogeneous catalysts, which, in turn, can result in easier set up of the reactions and separation of some metal catalysts from reaction mixture. In this assumption we have chosen some arenes with the alkyl side groups as the substrate that have been already proven as susceptible to microwave assisted oxidation [9] and tried to oxidize them using tungstoboric acid - HBW (i.e., homogeneous conditions) and HBW supported at SiO₂.

EXPERIMENTAL

Heterogeneous catalyst synthesis

The synthesis of catalyst was carried out using sol-gel method [10]. Distilled water was added (13mL) to a solution of tetraethoxysilane (45mmol) in ethyl alcohol (10,5mL). Then the solution was acidified with concentrated HNO₃ up to pH = 3 and stirred for 2h. Next H₄O₄₀BW₁₂(HBW) was added (1,05mmol) and the solution was stirred for another 3h. The final mixture was left at room temperature to crosslink for 4-5 days and then finely grounded

and dried at 100°C. The catalyst was characterised by means of the amount of tungsten (using AAS method), its distribution at the surface (SEM/EDS). Thermal behaviour and FT-IR analysis was also done.



Scheme 1: Oxidation of some aromatics by H₂O₂

All the reaction was carried out according to the Scheme 1 as follows:

Homogeneous reaction

The substrate (1,5mmol) was dissolved in 20mL of acetonitrile. Then 0,025mmol of H₄O₄₀BW₁₂ (HBW) and 12mmol of H₂O₂ (1,2mL of 30% water solution) was added to the solution. The mixture was heated conventionally or irradiated by microwaves (*Plazmatronika, Poland*, max. power 600W, applied power up to 35%) up to the boiling point and than kept at reflux for time indicated in Table 1. After the reaction, the mixture was cooled and extracted with diethyl ether. The organic layer was evaporated and crude product was purified by means of preparative HPLC (methanol: water 80:20, detection UV at 254nm). The structure of the product was proved by IR, HNMR and MS method.

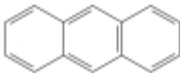
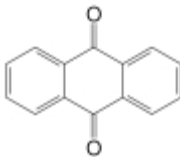
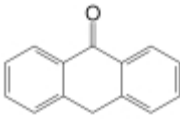
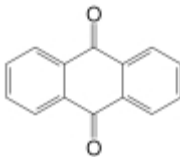
Heterogeneous reaction

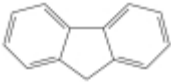
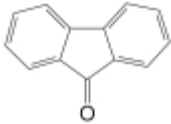
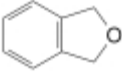
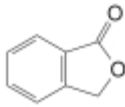
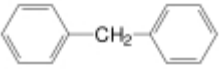
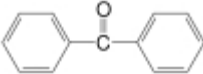
The substarte (1,5mmol) was dissolved in 20mL of acetonitrile and the catalyst was added to the solution. The amount of catalyst was calculated according to tungsten content in the sample estimated by AAS method. The concentration of tungsten was set up to the same level at in the homogeneous condition. Next 12mmol of H₂O₂ (1,2mL of 30% water solution) was added to teh mixture and it was heated conventionally or irradiated in microwave reactor (*Plazmatronika, Poland*, max. power 600W, applied power up to 35%) up to the boiling and than kept at reflux for time indicated in Table 1. After the reaction the system was cooled and the catalyst was separated by filtration. The liquid was extracted with diethyl ether and treated as in homogeneous reaction.

RESULTS AND DISCUSION

As a reasult of oxidation reactions, we have obtained a series of carbonyl compounds with yields listed in Table 1.

Table 1. Oxidation os some aromatics by H₂O₂ using tungsten catalyst.

Substrate	Product	Time [min]	Yield in HBW catalysed reaction [%]		Yield HBW/SiO ₂ catalysed reaction [%]	
			Conventional	Microwave	Conventional	Microwave
		15	43	85	92	96
		15	70	98	98	97

		120	29	47	39	57
		30	46	74	50	80
		120	19	40	16	45

The results clearly show that microwave irradiation improves the oxidation, and yields are higher than those from conventional experiments. The best yields are obtained in the cases of anthracene and 1,3-dihydrobenzofuran, and they do not depend on the applied catalytic system. From the other hand, the heterogeneous reactions are characterized by higher effectiveness than homogeneous reactions even though we compared conventional processes. It seems to be a consequence of SiO₂ matrix interaction which could also play a catalyst role for presented reaction. For example, applying silica catalyst without HBW for the oxidation of 1,3-dihydrobenzofuran, the product was afforded with 25% and 34% yield after 60 min. under conventional and microwave conditions, respectively. Thus, silica matrix interactions can play an important role in microwave assisted reactions because SiO₂ systems with supported heteropolyacids are known [10] for their interaction with microwaves. Such properties are responsible for rapid heating of the catalyst surface and overheating of active centers.

In conclusion, we can state that described microwave assisted processes of the oxidation of some alkyl substituted arenes give higher reaction yields under both homogeneous and heterogeneous conditions in comparison with conventional processes. The reactions can be further improved by supporting the catalysts onto silica matrix, which results in simplification of the reaction set up (post-process separation of catalyst) as well as in even higher reaction yields.

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