[e008]

Influence of microwave irradiation on the rate of complex chemical reactions.

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Abstract

A summary of detailed studies of influence of microwave irradiation on the kinetics of Knoevenagel condensation was presented. General conclusions were outlined.

Introduction

The Knoevenagel condensation is one of the important methods for the coumarins synthesis[1]. Recently, the influence of microwave irradiation on the kinetic of such reactions was investigated and an increase of the reaction rate under microwave conditions was observed[1-3]. In order to explain the origin of such an effect, the mechanism of these kinds of reactions was elucidated (Figure 1.)[4]. Based on detailed kinetics studies and taking into consideration the mechanism of the reaction the origin of microwave effect was discussed.
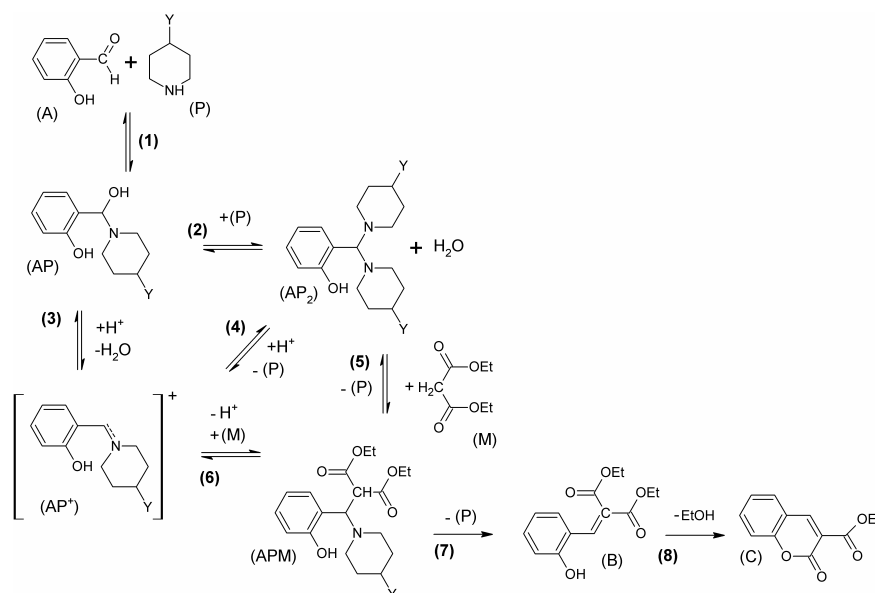

Figure 1. Mechanism of the condensation of salicylaldehyde with diethyl malonate in a nonpolar solvent catalyzed by secondary amines. For more details see ref.[4].

Results and discussion

Detailed study on the influence of microwave irradiation on the Knoevenagel condensation was carried out. The reactions were investigated both in polar (ethanol) and nonpolar (toluene) solvent with various initial concentrations of the substrates (E1…T5). The most significant differences between calculated and determined concentration were noted for T1 system. In other cases δ values were similar.

It seems that microwave irradiation does not accelerate the reaction. In the polar solvent (E1,E2) or in excess of one of substrate (T2, T3) and also when initial concentration of the substrates is high (T4) microwave energy is absorbed first of all by polar molecules and dissipated as a thermal movements. Only when concentration of reagents is lower (T1) the microwave effect may be considered. It is not clear why application of different catalyst – PP (T5) causes that microwave effect is not observable. It was found that the reaction rate depend on the concentration of water[4]. Removing of the water shifts equilibrium of aminal (AP2) formation to the right side and thus increases of overall reaction rate. Microwave irradiation may intensify the evaporation process and accelerate the reaction. In the case of less hygroscopic catalyst (PP) the 'removing water effect' could be less important and from that reason the difference δ is neglible (T5).

Table 1. Details of kinetics experiments.

Reaction system	Solvent	$[A]_0$	$[M]_0$	[catalyst]	Experimental rate equation
E1	Ethanol	0.18	0.18	[P]=0.05	$-\dfrac{d[X]}{dt}=k_{obsE1}[X]^2,\quad [A]=[M]=[X]$
E2	Ethanol	1.56	0.11	[P]=0.05	$-\dfrac{d[M]}{dt}=k_{obsE2}[M]$
T1	Toluene	0.18	0.18	[P]=0.05	$-\dfrac{d[X]}{dt}=k_{obsT1}[X]^2,\quad [A]=[M]=[X]$
T2	Toluene	1.22	0.11	[P]=0.04	$-\dfrac{d[M]}{dt}=k_{obsT2}[M]$
T3	Toluene	1.56	0.11	[P]=0.04	$-\dfrac{d[M]}{dt}=k_{obsT3}[M]$
T4	Toluene	1.30	1.30	[P]=0.03	$-\dfrac{d[X]}{dt}=k_{obsT4}[X]^2,\quad [A]=[M]=[X]$
T5	Toluene	0.36	0.36	[PP]=0.09	$-\dfrac{d[X]}{dt}=k_{obsT5}[X]^2,\quad [A]=[M]=[X]$

Table 2. Summary of the results of conventional and microwave experiments.

Reaction system	Heating mode[1]	δ [2]
E1	Δ	2
E1	MW	5
E2	Δ	2
E2	MW	3
T1	Δ	16
T1	MW (27)	27
T1	MW (150)	25
T2	Δ	3
T2	MW (150)	-4
T2	MW (150)	4
T3	Δ	5
T3	MW	3
T4	Δ	-9
T4	MW	-18
T5	Δ	2
T5	MW (255)	6

[1] Δ – conventional, MW (Power) – microwaves

[2] Relative difference between calculated and determined final concentrations of the reaction product – see Experimental part.

Conclusion

To elucidate influence of microwave irradiation on chemical reactions kinetics a few conditions should be fulfill:

- the reaction mechanism and all factors influenced to reaction rate should be know,
- the temperature during microwave experiments should be carefully controlled and measured,
- concentration of polar molecules both solvent and the reagents should be possibly low to avoid of microwave energy dissipation and shielding of a reaction intermediates by the polar molecules against microwave beam,
- intensity of microwave field should be highest as possible (additional external cooling may be applied).

Experimental part

Piperidine (P) was heated with solid potassium hydroxide for 5 h under reflux condenser. Then it was distilled and stored in a closed vessel. 4-Piperidinopiperidine (PP) (98% *Aldrich*) was recrystallized from hexane. Salicyl aldehyde (A) (>99% *Fluka*), diethylmalonate (M) (>99% *Fluka*) and toluene (*POCH*) were used as received.

The progress of reactions was monitored by a gas chromatograph *Agilent 6850* with flame ionization detector (FID) fitted with *HP-1* columns. The reactions were carried out in a single-mode microwave reactor with a continuous power regulation (SynthWave 402, Prolabo) equipped with magnetic stirrer. To control temperature the fiber-optics tip of the thermometer (ReFlex, Nortech) was inserted directly into the reaction mixture.

Reaction kinetics

The consumption of the substrates rates equations and reactions rate constants were experimentally determined for reactions carried out in ethanol (E) and toluene (T) as solvents and for various initial concentrations of the substrates (Table 1). Based on isothermal kinetics experiments run at different temperatures under conventional heating Arrhenius parameters were determined for each reaction system (E1…T5).

Microwave experiments

An appropriate amount of the substrates, the catalyst (P or PP) and naphthalene (internal standard) were dissolved in toluene in a tube. The tube was placed inside the microwave rector. The reaction mixture was stirred during irradiation by stirring bar and temperature was carefully measured and recorded by a computer. At appropriate time intervals, a sample of the mixture was withdrawn and the reaction progress was monitored by means of GC-FID. Based on saved temperature profile, Arrhenius parameters and material balance concentrations of the reaction product were calculated $[C]_{calc}$ and compared to those determined experimentally $[C]$:

$$\delta = \frac{[C]_{calc} - [C]}{[C]} \times 100\%$$

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