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Comparative study on isothermal kinetics of fullerol formation under conventional and microwave heating

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Abstract

The kinetic of fullerol formation in the presence of cetyl trimethyl ammonium bromide (CTAB) as a phase transfer catalyst both under conventional and microwave heating conditions was investigated. It was found that the activation energy (E_a) for the investigated processes under microwave heating was two to four times lower than for the same, conventionally heated process. Also, the pre-exponential factor ($\ln A$) was 436–4200 times lower for the microwave heating process. The differences in the kinetic parameters (activation energy and pre-exponential factor) of the process under microwaves can be explained with the specific (non-thermal) activation of centres of the newly formed phase due to the electromagnetic energy absorption.

Keywords: Fullerol; Kinetics; Microwave irradiation; Activation energy; Phase transfer catalyst

1. Introduction

Chemical and physical properties of fullerene C_{60}, the most representative among fullerenes, which are due to its unusual structure and extended π-electron system, have stimulated the synthesis of a large number of derivatives with different targets, achieving promising results [1]. C_{60}-fullerols are one of the most interesting fullerene derivatives of fullerene chemistry. They have potential applications in aqueous solution chemistry, electrochemistry, material chemistry and biochemistry. Fullerols have been used as preparatory material for syntheses of dendritic star-shaped polymers [2] and hypercrosslinked networks, as probes for investigating the surface properties of biomaterials [3] and as coatings for solid-phase microextraction [4]. Also, they exhibited excellent free-radical scavenging abilities against reactive oxygen species and radicals under physiological conditions [5,6].

Different methods have been developed to synthesize water-soluble C_{60}. C_{60}-fullerols can be obtained either directly from C_{60} [7] or from their derivatives [8]. Some of the most published methods involve the hydrolysis of a fullerene intermediate made by nitronium chemistry [9], aqueous acid chemistry [10], oleum [11], nitrogen dioxide radicals [12], hydroboration [13] or by hydrolysis of polycyclosulfated precursors [14]. A much simpler method of polyhydroxylation involves the reaction of an aqueous NaOH solution in contact with a toluene or benzene solution of C_{60} in the presence of a phase transfer catalyst. Phase transfer is usually accomplished with tetrabutylamonium hydroxide [7], cetyl trimethyl ammonium bromide (CTAB) [3] or polyethylene-glycol [15]. Recently, synthesis of C_{60}-fullerenes via solid state mechano-chemical reaction with potassium hydroxide under high-speed vibration milling conditions was reported [16]. This approach eliminates the use of organic solvents.

The use of microwave irradiation as an alternative heat source is becoming more and more frequently used in chemistry [17]. One of the main advantages of the use of microwave heating in chemical synthesis is significantly faster reaction rates. In "fullerene" chemistry the microwave irradiation was applied for preparation of fullerene C_{60} derivatives by cycloaddition [18]. Moreover, a microwave irradiation was applied to synthesize derivatives of fullerene C_{60} in the reaction systems which used phase transfer catalyst but without organic solvent [19].

Numerous observations of enhanced solid-state reaction rates during microwave heating: nucleation and crystallization [20–23], grain growth [24], annealing [2,25], ceramics [26],

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combustion synthesis [27], calcination [28], and other solid-state reactions [29] have been reported in literature. These observations of the enhancements of the reaction rates under the influence of microwaves generally have been named as "the microwave effect" [18,30]. In the past, these claims have created significant controversy, partly due to the lack of credible and theoretical explanations.

In the present study, the isothermal kinetics of fullerol ($C_{60}(OH)_{24}$) formation in the presence of cetyl trimethyl ammonium bromide (CTAB) as a phase transfer catalyst (PTC) under the conventional and microwave heating of the reaction mixture was investigated and compared.

2. Experimental

2.1. Materials

Fullerene (C_{60}) 99.95%, was supplied by MER Corp, Tucson, USA. Benzene, p.a., was purchased from GR Lach-Ner, Czech Republic. Sodium hydroxide and ethanol, both of p.a. purity were obtained from Merck-Darmstadt, Germany. Cetyl trimethyl ammonium bromide (CTAB) p.a. was purchased from Sigma Aldrich Co., USA.

2.2. General procedure of fullerol preparation

The fullerol was prepared following the modified procedure of Zhao et al. [3]. That process consists in follows. A deep violet benzene solution of C_{60} (50 mg of C_{60} in 50 ml of benzene) was added drop wise to the aqueous solution of NaOH (2 g in 20 ml of water) containing 10 mg of CTAB and fives drops of H_2O_2 (30%). The obtained suspension was placed in a thermostated water bath at a desired temperature (20, 25, 30, 35 and 40 °C ± 0.2 °C) or in a microwave reactor (at 20, 25, 30, 40 and 50 °C ± 0.2 °C). The mixture was stirred vigorously with a magnetic stirrer (at 500 r/min) until the organic layer became colourless. At predetermined reaction intervals samples were withdrawn from the organic layer of the reaction mixture and analysed by VIS spectrometry. When the organic layer became colourless it was separated from the reddish-brown coloured aqueous phase and the obtained product was precipitated by adding ethanol to the aqueous solution. This step was repeated several times (at least three times) to ensure complete removal the impurities of NaOH and CTAB. The precipitate was dried at 60 °C for 5 h. The final product was a dark brown solid. In the case of microwave-assisted synthesis, the prepared reaction mixture was placed in a focused microwave reactor (Discover, CEM Corporation, Matthews, NC, USA) supplied with a programmed temperature control system. All the reactions were carried out in the microwave field of 2.45 GHz. The used microwave reactor was modified so the device for maintaining the constant temperature of the reaction mixture by cooling with dry nitrogen was introduced in it. On that way, by simultaneously cooling of the reaction mixture and varying the input power of the microwave field temperature was maintained to be constant within the limitation (±0.2 °C) during the experiments. For the additional temperature's control we used the so called method of rapid dipping of a thermocouple. Namely, after a microwave irradiation of the reaction mixture, a thermocouple was submersed and the temperature of the reaction mixture was measured.

2.3. Methods of analysis

2.3.1. VIS spectra

VIS spectra's of both C_{60} solution in benzene and the reaction's mixtures organic layer were obtained using UV–vis spectrometer, Cintra 10e, Serial No. V 3163, UK.

2.3.2. Elemental analysis

The determination of carbon [C (%)] and hydrogen [H (%)] contents in the final reaction product was performed on a Carlo Erba Elemental Analyzer, type EA 1108, Italy.

2.3.3. Infrared spectra

The IR spectra of the prepared fullerol samples were recorded in the form of KBr pellets (1 mg of sample to 100 mg KBr) using a Bomem MB 100 Fourier transform infrared spectrometer (FT-IR), Hartmann & Braun, Canada.

2.4. Determination of the degree of transformation of fullerene to fullerol

The C_{60} benzene solution was deep violet in colour and had two characteristic absorption maximums at $\lambda_1 = 538$ nm and $\lambda_2 = 592$ nm. During the reaction of fullerol formation, the intense colour of the C_{60} benzene solution reduced due to the decrease of fullerene concentration in the reaction mixture. The degree of transformation of C_{60} to $C_{60}(OH)_{24}$ at time (t), can be calculated using the following equation:

$$\alpha = \frac{C_0 - C_i}{C_0} \tag{1}$$

where C_0 is the starting concentration of C_{60} in the benzene solution and C_i is the concentration of C_{60} in the organic layer of the reaction mixture at a definite reaction time (t). The C_{60} concentration was determined by measuring the absorption at $\lambda = 538$ nm and checking with the Beer's law.

2.5. Determination of the number of hydroxyl groups

The number of hydroxyl groups (n(OH)) was determined according to the method presented in the work of Goswami et al. [31], using the following equation:

$$n_{\mathrm{OH}} = \frac{M_{\mathrm{C}_{60}}}{C} \times \frac{\Delta m}{M_{\mathrm{OH}}} \tag{2}$$

where $M_{\mathrm{C}_{60}}$ and M_{OH} are molar masses of C_{60} and hydroxyl (OH), C (%) the carbon content in the sample, and Δm (%) is the weight loss of the sample at temperatures between 150 and 570 °C. The weight losses of samples were determined by gravimetrically measuring the weight of sample heated at $T_1 = 150$ °C until constant weight and after that at $T_2 = 570$ °C again until constant weight. The weight difference between these two weights represented Δm.

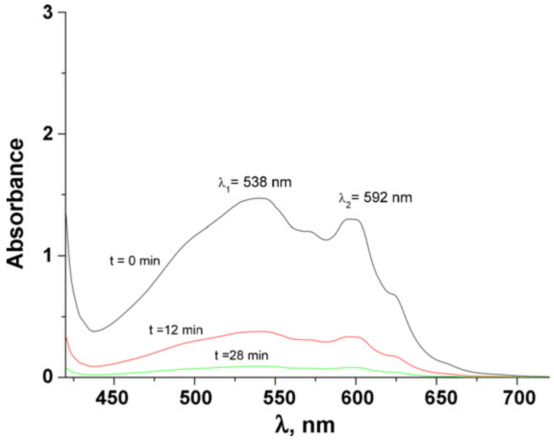

Fig. 1. VIS spectra of the fullerene–benzene solution and organic layer of reactions mixture during fullerol forming.

3. Results and discussion

Fig. 1 presents a VIS spectrum of fullerene benzene solution and selected samples of spectres of organic layer of the reaction mixture during reaction of fullerol forming by conventional heating at 40 °C. As can be seen from the presented results, during the reaction of fullerol forming, intensities of the absorption maximums at $\lambda_1 = 538$ nm and $\lambda_2 = 592$ nm decreases due to the formation of fullerol and its shift to the aqueous phase of the reaction mixture.

The elemental analysis of the final products of the reactions obtained at different temperatures both for processes under conventional (con) and microwave (mw) heating was performed. The effect of reaction temperature on carbon (C), hydrogen (H) and weight loss (Δm) of the final products synthesised under the conventional and microwave heating, is shown in Table 1.

The results of the elemental analysis reveal that all the final products had the same content (C: 64.0%, H: 2.15%) and gave the almost same weight loss ($\Delta m \approx 36\%$). Based on the obtained results, it may be concluded that all of the formed products had the same empirical formula: $C_{60}(OH)_{24}$.

The IR spectra of all the final products had the same shape and showed characteristic features for the IR spectra of fullerol: a broad hydroxyl group related absorption band centred at 3430 cm^{-1}, two C=C bands (at 1585 and 1358 cm^{-1}) and a C–C stretching bands at 1065 and 1016 cm^{-1}. Fig. 2 shows an example of typical IR spectrum of the reaction product obtained in the reaction under microwave heating at 40 °C.

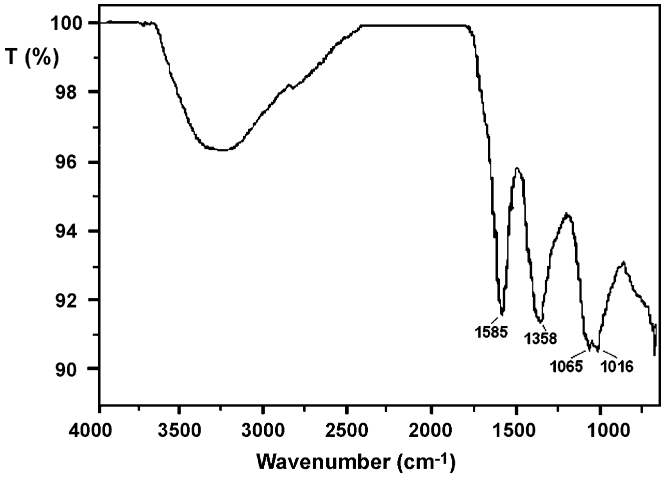

Fig. 2. The IR spectrum of the obtained product under microwave heating at 40 °C.

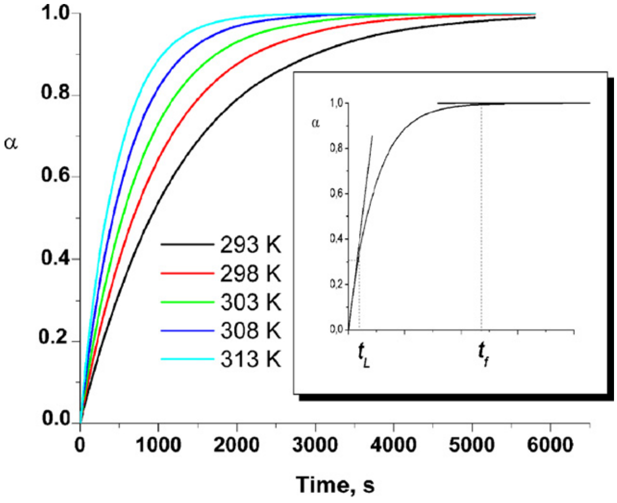

Fig. 3. The isothermal conversion curves of fullerol formation under conventional heating and graphical determination of t_L and t_f (inset).

Figs. 3 and 4 show the isothermal changes of the degrees of transformation of fullerene (C_{60}) to fullerol ($C_{60}(OH)_{24}$) with reaction time (conversion curves) at different temperatures for conventional and microwave heating, respectively.

Conversion curves, both for conventional and microwave heating, are similar by shape at all of the reaction temperatures.

Table 1
Temperature influence on the results of the elemental analysis and weight loss of the reaction's final product

T (K)	C_{con} (%)	C_{mw} (%)	H_{con} (%)	H_{mw} (%)	Δm_{con} (%)	Δm_{mw} (%)	$n(OH)_{con}$	$n(OH)_{mw}$
293	64.0	64.2	2.13	2.14	36.30	36.40	24	24
298	64.0	64.0	2.15	2.15	36.28	36.28	24	24
303	63.9	64.1	2.13	2.13	36.21	36.35	24	24
308	63.8	–	2.14	–	36.16	–	24	24
313	63.9	64.0	2.17	2.17	36.21	36.26	24	–
323	–	63.9	–	2.13	–	36.21	–	24

Table 2
Temperature influence on the specific parameters of the conversion curves for the conventional and microwave process

T (K)	Conventional process				Microwave process			
	t_L^{con} (s)	v_{in}^{con} ($\times10^{-4}$ s^{-1})	t_f^{con} (s)	v_f^{con} ($\times10^{-4}$ s^{-1})	t_L^{mw} (s)	v_{in}^{mw} ($\times10^{-4}$ s^{-1})	t_f^{mw} (s)	v_f^{mw} ($\times10^{-4}$ s^{-1})
293	600	0.62	4600	2.20	180	20.9	2100	4.76
298	600	0.78	4000	2.50	180	22.7	1920	5.21
303	600	0.92	3600	2.80	180	23.4	1860	5.38
308	600	1.08	3000	3.30	–	–	–	–
313	600	1.24	2400	4.20	180	28.7	1620	6.17
323	–	–	–	–	180	26.1	1320	7.58

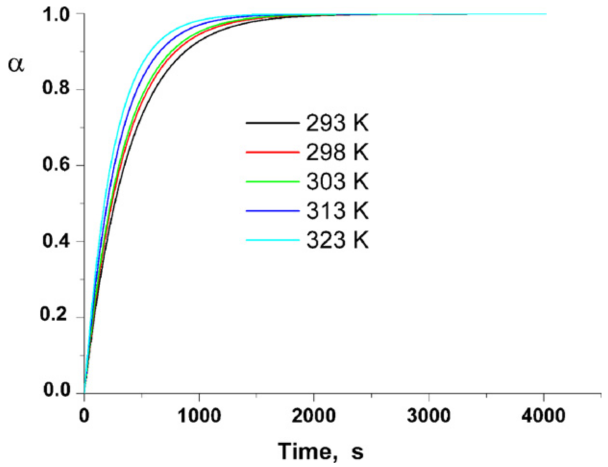

Fig. 4. The isothermal conversion curves of fullerol formation under microwave heating.

Three distinct stages of the changes of the degrees of transformation of fullerene (C_{60}) with time can be clearly observed on the presented conversion curves, i.e., a linear, non-linear and saturation stage. In order to determine the influence of temperature on the shape of the conversions curves, the so called specific shape parameters of the conversion curves were defined: the period of linearity (t_L), the initial reaction rate (v_{in}), the saturation time (t_f) and the saturation reaction rate (v_f). The period of linearity (t_L) is the time interval within which the conversion degree (α) increases linearly with the reaction time. The initial reaction rate was calculated as

$$v_{in} = \frac{\alpha_L}{t_L} \tag{3}$$

where α_L is the degree of conversion at the end of the period of linearity which is graphically determined (Fig. 3). The saturation time (t_f) is defined as the time at which the maximal conversion degree at a defined temperature is reached for the first time. The saturation reaction rate (v_f) is defined by

$$v_f = \frac{1}{t_f} \tag{4}$$

The changes of the parameters of the conversion curves (t_L, v_{in}, t_s, v_f) with temperature are given in Tables 2 and 3 summarized the kinetic parameters calculated based on them.

Based on the results shown in Table 2, it can be easily seen that as the temperature increase, the saturation reaction time (t_f^{con} and t_f^{mw}) decrease both for the conventionally and microwave heated processes. On the contrary however, the initial (v_{in}^{con} and v_{in}^{mw}) and saturation reaction rates (v_f^{con} and v_f^{mw}) increase as temperature increases for both process. As might be expected, the initial and saturation reaction rates were higher for microwave heated reactions. Since the increase of initial and saturation reaction rate with temperature is exponential, the kinetic parameters (activation energy and pre-exponential factor) for both the initial and saturation stage of fullerene transformation to fullerol can be determined by applying the Arrhenius equation. The obtained results are shown in Table 3.

Based on the obtained results presented in Table 3, it can be seen that the activation energy of the initial stage ($E_{a,in}^{con}$) of C_{60} transformation to $C_{60}(OH)_{24}$ was identical to the activation energy of the saturation stage ($E_{a,in}^{con} = E_{a,f}^{con} = 26 \pm 1\,\mathrm{kJ/mol}$) of a conventional process, while the value of the pre-exponential factor of the initial stage was somewhat higher ($\ln A_{in}^{con} = 3.2 \pm 0.4\,\mathrm{s}^{-1}$) than the pre-exponential factor for the saturation stage of the conventional process. The activation energies for both the initial stage ($E_{a,in}^{mw}$) and saturation stage ($E_{a,f}^{mw}$) for the microwave process were significantly lower then E_a for the conventional process, and $E_{a,in}^{mw}$ (8 ± 1 kJ/mol) was lower than $E_{a,f}^{mw}$ (12 ± 1 kJ/mol). On the contrary however, the pre-exponential factors were found to be the same for the initial stage and saturation stage of the process in a microwave field

Table 3
The kinetic's parameters calculated from the methods of initial and saturation rate, for the conventional and microwave process

Conventional process				Microwave process			
Initial stage		Saturation stage		Initial stage		Saturation stage	
$E_{a,in}^{con}$ (kJ/mol)	$\ln A_{in}^{con}$ (s^{-1})	$E_{a,f}^{con}$ (kJ/mol)	$\ln A_f^{con}$ (s^{-1})	$E_{a,in}^{mw}$ (kJ/mol)	$\ln A_{in}^{mw}$ (s^{-1})	$E_{a,f}^{mw}$ (kJ/mol)	$\ln A_f^{mw}$ (s^{-1})
26 ± 1	3.2 ± 0.4	26 ± 1	1.3 ± 0.3	8 ± 1	-2.9 ± 0.2	12 ± 1	-2.9 ± 0.2
$r^a = -0.997$		$r^a = -0.984$		$r^a = -0.997$		$r^a = -0.987$	

[a] Linear correlation coefficient.

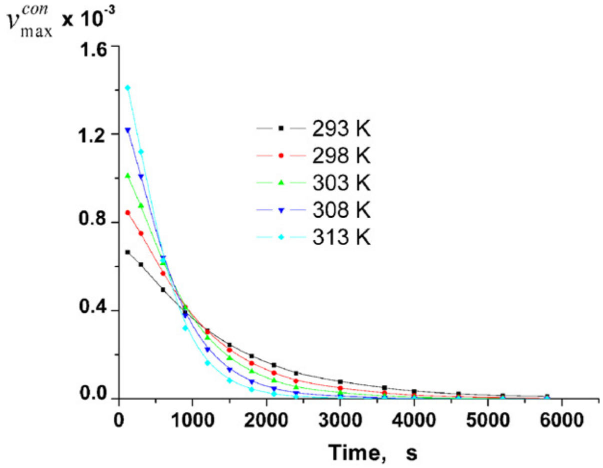

Fig. 5. The isothermal reaction's rate changes with reaction time (conventional heating).

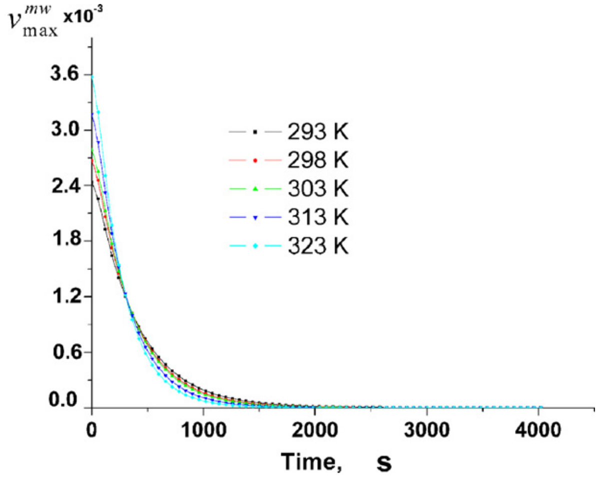

Fig. 6. The isothermal reaction's rate changes with reaction time (microwave heating).

($\ln A_{\text{in}}^{\text{mw}} = \ln A_{\text{f}}^{\text{mw}} = -2.9 \pm 0.2\,\text{s}^{-1}$), but they were still significantly lower than the values of $\ln A$ for the conventional process.

In order to obtain the kinetic parameters by the maximal rate method, the changes of reaction rates of fullerol formation with time were determined from the experimentally determined isothermal conversion curves and the maximal rates were found. Isothermal reaction rates were calculated using Microcal Origin software.

The isothermal changes of the reaction rates with reaction time for the conventional and microwave heated process are shown in Figs. 5 and 6, respectively.

As can be seen from the results presented in Figs. 5 and 6, the rate of fullerol formation decreased with reaction time both for conventional and microwave heating, at all of the investigated temperatures. The maximal reaction rates of fullerol formation may be observed at the initial stages of the process. The established change in the rate of fullerol formation with time is characteristic of the so called decelerator process and their corresponding kinetic models (F1; R2; R3) [32].

Table 4 shows the temperature's influence on the maximum reaction rate ($v_{\text{max}}^{\text{con}}$, $v_{\text{max}}^{\text{mw}}$) and on the kinetic's parameters (activation energy and pre-exponential factor) for conventional and microwave heated process of fullerol formation.

Since the maximum reaction rate both for the conventional and microwave heated process ($v_{\text{max}}^{\text{con}}$ and $v_{\text{max}}^{\text{mw}}$) increases exponentially with temperature, the kinetic parameters of fullerene transformation to fullerol (activation energy and pre-exponential factor) were determined using the Arrhenius equation. It was found that the maximal activation energy for the conventional process $E_{\text{a,max}}^{\text{con}}$ was (29 ± 1 kJ/mol), which was in correspondence with the value for activation energy of the initial stage $E_{\text{a,in}}^{\text{con}}$ (26 ± 1 kJ/mol) and $\ln A_{\text{max}}^{\text{con}}$ ($4.6 \pm 0.4\,\text{s}^{-1}$). The maximal activation energy for the microwave process ($E_{\text{a,max}}^{\text{mw}}$) is exactly between the $E_{\text{a,in}}^{\text{mw}}$ (8 ± 1 kJ/mol) and $E_{\text{a,f}}^{\text{mw}}$ (12 ± 1 kJ/mol).

Because the kinetic parameters determined by different methods significantly differ one from another, to determine their real values the "model-fitting" method was applied to establish the kinetic's model for the formation of fullerol from the C_{60} benzene solution in the presence of CTAB.

The appropriate kinetic model was determined by comparing (graphically and analytically) the experimentally obtained function $\alpha_e = f(t_N)$ with the theoretical functions $\alpha = f(t_N)$ for different solid state reaction models. The normalized time (t_N) was determined using the following equation:

$$t_N = \frac{t}{t_{0.9}} \qquad (5)$$

where $t_{0.9}$ is the reaction time at $\alpha = 0.9$. The set of kinetic reaction models used to determine the model of the investi-

Table 4
Temperature influence on reaction rate and on the kinetic's parameters, for conventional and microwave heated process

T (K)	Conventional process	Microwave process	Kinetic parameters			
	$v_{\text{max}}^{\text{con}}$ ($\times 10^{-3}\,\text{s}^{-1}$)	$v_{\text{max}}^{\text{mw}}$ ($\times 10^{-3}\,\text{s}^{-1}$)	$E_{\text{a,max}}^{\text{con}}$ (kJ/mol)	$\ln A_{\text{max}}^{\text{con}}$ (s^{-1})	$E_{\text{a,max}}^{\text{mw}}$ (kJ/mol)	$\ln A^{*\text{mw}}$ (s^{-1})
293	0.66	2.4	29 ± 1	4.6 ± 0.4	10 ± 1	-1.8 ± 0.2
298	0.84	2.7				
303	1.01	2.8				
308	1.22	–				
313	1.41	3.2	$r^a = -0.997$		$r^a = -0.994$	
323	–	3.6				

[a] Linear correlation coefficient.

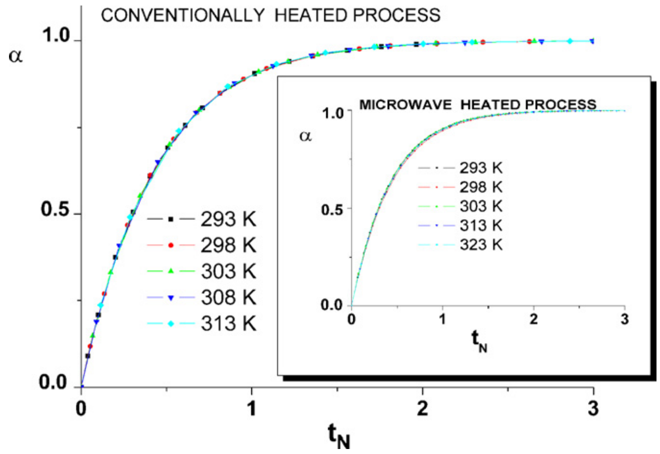

Fig. 7. The isothermal change of the degrees of fullerene transformation to fullerol (α) with t_N, under conventional and microwave heating.

gated reaction was undertaken from the work of Vyazovkin and Wight [33]. Fig. 7 presents the isothermal dependences of the degree of C_{60} transformation to fullerol (α) on t_N (normalized kinetic curves) at different temperatures for the conventional and microwave process.

The isothermal curves of the changes of the degree of fullerene transformation to fullerol (α) with t_N, both at conventional and microwave heating at all of the investigated temperatures were identical. The established invariability of the isothermal changes of α with t_N represents a direct proof of the unique mechanism and kinetic model of the investigated reaction.

For example, Fig. 8 shows the plot of $\alpha = f(t_N)$ for the selected theoretical kinetic models (solid curves) and the experimental plots of $\alpha = f(t_N)$ for fullerol formation under microwave heating at all of the investigated temperatures. According to these results, it can be stated with great assurance that F1 would be the best model to describe the kinetics of fullerol formation at all of the investigated temperatures. This corresponds to the kinetics of first-order chemical reactions:

$$-\ln(1-\alpha) = k_M t \quad (6)$$

where k_M is a model constant for the first-order chemical reaction rate. The isothermal dependences of $[-\ln(1-\alpha)]$ versus reaction time for fullerol formation at different temperature are shown in Figs. 9 and 10 for the microwave and conventional heating, respectively. The dependence of $[-\ln(1-\alpha)]$ on time at all of the investigated temperatures gave straight lines. For both conventional and microwave processes, from the slopes of these linear dependences, the model's reaction rate constants (k_M) were determined.

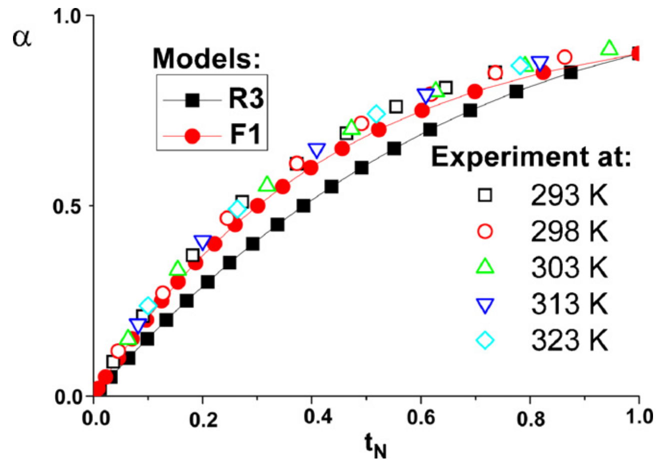

Fig. 8. The plot of $\alpha = f(t_N)$ for the selected theoretical reaction models (R3 (■) and F1 (●)) and the experimental plots of $\alpha = f(t_N)$ at all investigated temperatures for microwave heated process.

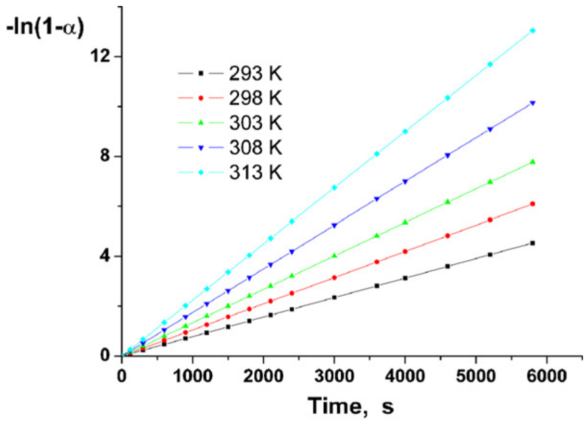

Fig. 9. Isothermal change of $[-\ln(1-\alpha)]$ with time for conventional heating.

The temperature influence on k_M is shown in Table 5. Since the temperature dependence of the model kinetic constant for the reaction rate was expressed by the Arrhenius equation, the kinetic model's parameters (model activation energy and pre-exponential factor) of fullerol formation were determined. The obtained results are also given in Table 5.

All the methods applied for calculating the kinetic parameters gave much lower activation energies and pre-exponential factors for microwave heating than the corresponding values calculated for conventional heating.

The activation energy for the microwave-heated process is from 2.2 times (maximal rate method) to 3.6 times (model-fitting method) lower than the activation energy for the convention-

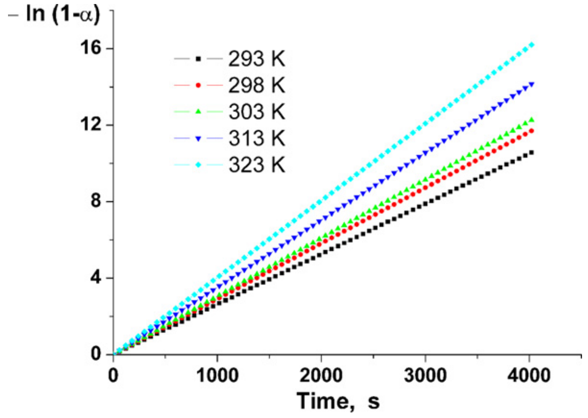

Fig. 10. Isothermal change of $[-\ln(1-\alpha)]$ with time for microwave heating.

Table 5
Temperature influence on the model's reaction rate constant and the kinetic parameters

T [K]	Conventional process	Microwave process	Kinetic parameters			
	k_M^{con} ($\times 10^{-3}$ s^{-1})	k_M^{mw} ($\times 10^{-3}$ s^{-1})	$E_{a,M}^{con}$ (kJ/mol)	ln A_M^{con} (s^{-1})	$E_{a,M}^{mw}$ (kJ/mol)	ln A_M^{mw} (s^{-1})
293	0.78	2.63	40 ± 1	9.3 ± 0.2	11 ± 1	-1.4 ± 0.2
298	1.1	2.91				
303	1.34	3.06				
308	1.75	–				
313	2.25	3.52	$r^a = -0.997$		$r^a = -0.998$	
323	–	4.05				

[a] Linear correlation coefficient.

ally heated process. Also, the pre-exponential factor for the microwave process is 436 times (maximal rate method) to 4200 times (model-fitting method) lower than the pre-exponential factor for the conventional process. To explain the "microwave effect" on remarkable increase of the reaction rate of fullerol formation using microwave heating, as opposed to conventional heating, the effect of microwave heating on temperature, activation energy and pre-exponential factor of the investigated process were considered.

The calculated values of the isothermal constants rate and the kinetic parameters, under conventional and microwave heating of the reaction system, enables the investigation of the influence of microwave heating on the reaction rate. If it was assumed that under microwave heating the Arrhenius dependence was valid, which was already confirmed in this work, it was easy to get to the expression:

$$Z = \frac{k^{mw}}{k^{con}} = \frac{A^{*mw} \exp(-E^{*mw}/RT^{mw})}{A^{con} \exp(-E^{con}/RT^{con})} \tag{7}$$

where T^{mw} and T^{con} are temperatures of the reaction system under the microwave heating and conventional heating, respectively and E_a^{*mw} and A^{*mw} are the calculated values of the kinetic parameters under the microwave heating. If it was assumed that under the influence of microwave heating the kinetic parameters remained unchanged and only local over-heating was present, i.e., $E^{mw} = E^{con}$; $A^{mw} = A^{con}$; $T^{mw} \neq T^{con}$, then from Eq. (8), it was easy to calculate the reaction temperature at conditions of local over-heating:

$$T^{mw} = \frac{T^{con}}{(1 - \ln Z RT^{con}/E^{con})} \tag{8}$$

And the local over-heating can be calculated as

$$\Delta T = T^{mw} - T^{con} \tag{9}$$

The calculated values for T^{mw} and ΔT are listed in Table 5.

If it was assumed that $T^{mw} = T^{con}$; $E^{mw} = E^{con}$, then, on the basis of Eq. (7) it was easy to calculate the pre-exponential factors under microwave heating at any of the investigated temperatures:

$$A^{*mw} = ZA^{con} \tag{10}$$

The calculated values of $\ln A^{*mw}$ are given in Table 6. If $T^{mw} = T^{con}$ and $A^{*mw} = A^{con}$, then Eq. (7) transforms into:

$$E_a^{*mw} = E_a^{con} - RT^{con} \ln Z \tag{11}$$

based on which, the E_a^{*mw} value of the process under microwave heating could be calculated. The calculated values are listed in Table 6.

Calculated values for E_a^{mw} (38.3 kJ/mol) and $\ln A^{mw}$ (10.3 s^{-1}) were significantly different from the experimental values of E_a^{mw} (11 ± 1 kJ/mol) and $\ln A^{mw}$ (-1.4 ± 0.2 s^{-1}). Also, the reaction temperature for the microwave heated process (T^{mw}) appears to be different from the experimental temperature (T). This indicates that fullerol formation under microwave heating follows a different reaction path than the process of fullerol formation under conventional heating. The thermal activation of the process initiates the activation of a high number of low energy activation centres for the formations of the fullerol. This could explain the high value of $\ln A^{con}$ because this value is proportional to the concentration of activation centres. During the thermal activation the centres with lower energy are activated first. The activation energy E_a^{con} is higher than E_a^{mw} because activation energy is inversely proportional to the energy of the centres. On the contrary however, the microwave heating of the reaction mixture leads to the rapid energy transfer and absorption of the thermal energy. Due to that, energy of the centres increases which in turn leads to a non-equilibrium distribution which is characterized by the small number of centres with high energy. Accordingly, the value of $\ln A^{mw}$ is significantly lower than $\ln A^{con}$ (lower concentration of centres) and E_a^{mw} is lower than E_a^{con} (higher centres energy).

Therefore, the reaction of fullerol formation under the microwave heating is significant increased most probably due to the "microwave effect".

Table 6
The calculated kinetic parameters, T^{mw} and ΔT under the microwave heating of the reaction system

T (K)	k^{mw}/k^{con}	T^{mw} (K)	ΔT (K)	$\ln A^{*mw}$ (s^{-1})	E_a^{*mw} (kJ/mol)
293	3.32	316.3	22.7	10.6	37.6
298	2.76	317.7	19.7	10.4	38.0
303	2.38	320.3	17.3	10.3	38.3
313	1.81	321.5	13.5	10.1	38.8

4. Conclusion

The kinetic models for fullerol formation under conventional and microwave heating are identical.

The reaction rate of fullerol formation by microwave irradiation is two to four times higher than the reaction rate of fullerol formation under conventional heating.

In the presence of microwave heating fullerol formation is carried out along a reaction path with lower activation energy and a significantly lower pre-exponential factor.

The decrease of the kinetic's parameters (activation energy and pre-exponential factor) of fullerol formation under the microwave heating the reaction mixture, is a result of the specific (non-thermal) activation of the centres responsible for the fullerol formation.

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