Effect of Ultrasonic Field on Isothermal Kinetics of Fullerene Polyhydroxylation

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Abstract:
The isothermal kinetics of fullerene polyhydroxylation under ultrasonic field was investigated. The isothermal kinetic curves of fullerene polyhydroxylation at different temperatures ranging from 293 K to 313 K were determined. By application of the isoconversion method it was established that the reaction of fullerene polyhydroxylation with sodium hydroxide and cetyl trimethyl ammonium bromide as phase transfer catalyst was kinetically an elementary reaction.

The model-fitting method confirmed that the kinetics model of first-order chemical reaction best described the kinetics of fullerene polyhydroxylation under ultrasonic field and the kinetics parameters of fullerene polyhydroxylation were determined \( (E_a = 29 \text{ kJ/mol and } \ln A = 9.4 \text{ min}^{-1}) \).

It was established that the reaction rate of fullerene polyhydroxylation under ultrasonic field is higher from 1.5 times to 2.2 times than the rate of comparative reaction under the conventional heating. The activation energy is 28% lower than the value of activation energy determined under the conventional heating, whereas the value of pre-exponential factor is 40 times higher.

The decreased value of activation energy \( (E_a) \) and pre-exponential factor \( (\ln A) \) in the ultrasonic field is explained with the increase in the value of ground energy level of the resonant vibration mode \( (\nu = 500 \text{ cm}^{-1}) \) of \( C_{60} \) molecule \( (A_g(1) \text{ vibrational mode}) \) and toluene molecule (out-of plane bending C-C-C vibration) and with the decreased value of anharmonicity factor.

Keywords: Fullerene polyhydroxylation; Kinetics; Ultrasonic field.

1. Introduction

The most representative fullerene, \( C_{60} \), have unique chemical and physical properties due to its unusual structure and extended \( \pi \)-electron system [1]. Since, the pristine \( C_{60} \) is insoluble in water [2]. Numerous methods were developed to overcome the insolubility of \( C_{60} \), while retaining its unique inherent properties, through surface derivatization.

Polyhydroxylated \( C_{60} \) fullerenes (fullerols) are derivatives of \( C_{60} \) with hydroxyl group formed by chemical modification of covalent C-O bond on their surfaces. The chemical modification of fullerenes by incorporating OH groups on their carbon surface yields a variety of \( C_{60}(OH)_n \), \( (2 \leq n \leq 44) \) exhibiting different degrees of solubility in water [3].

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Compared with the pristine form, polyhydroxylated fullerenes have more potential applications due to their enhanced water solubility. It has been found that fullerols can: reduce cardiotoxicity of some drugs [4] and inhibit HIV-protease [5], hepatitis C virus [6] and abnormal growth of cells [7]. Furthermore, they exhibited excellent free-radical scavenging abilities against reactive oxygen species and radicals under physiological conditions [8, 9].

The most published synthetic paths of fullerene C$_{60}$ polyhydroxylation involves hydrolysis of a fullerene intermediate made by nitronium chemistry [10], aqueous acid chemistry [11], oleum [12], nitrogen dioxide radicals [13], hydroboration [14] or by hydrolysis of polycyclosulfated precursors [15]. A much simpler method of polyhydroxylation involves reaction in two phase system consisting a toluene or benzene solution of C$_{60}$ and aqueous NaOH, as hydroxylation agent, in presence of a phase transfer catalyst. Phase transfer is usually accomplished with tetrabutyl-amonium hydroxide (TBAH) [10, 16, 17, 18], cetyl trimethyl ammonium bromide (CTAB) [19] or polyethylene-glycol [20, 21]. Synthesis of water-soluble fullerene by interaction of mixture of strong inorganic acid (sulphuric and nitric acid) with fullerene C$_{60}$ assisted by ultrasonic field was presented in the article of Ko et al [22].

In the manuscript of Adnadević et al., a comparative analysis of the isothermal kinetics of fullerol C$_{60}$(OH)$_{24}$ formation under the conventional heating and microwave heating was performed. Based on the obtained results the authors concluded that the microwave heating leads to the significant increase in the rate of fullerol formation without changing the mechanism and the kinetics [23].

Keeping in mind that numerous chemical reaction under influence of ultrasonic field are significantly accelerated, in this manuscript the isothermal kinetics of fullerol formation under ultrasonic field was investigated with aim to determine: a) the kinetics model; b) the kinetics complexity of the polyhydroxylation reaction; c) the values of kinetics parameters and d) to explain the effects of ultrasonic field on the kinetics of fullerol formation.

2. Materials and methods

2.1. Materials

The following reagents were used: Fullerene (C$_{60}$) 99,95 %, produced by Mer, USA, Toluene p.a. purchased from GR Lach-Ner, Czech Republic, Sodium hydroxide (NaOH), Hydrogen peroxide (H$_2$O$_2$) and Ethanol of p.a. purity were obtained from Merck, Germany. Cetyl trimethyl ammonium bromide (CTAB), p.a. was purchased from Sigma Aldrich Co., USA.

2.2. Methods

2.2.1. Fullerene polyhydroxylation

The fullerol synthesis by the method of C$_{60}$ polyhydroxylation was described in the manuscript of Adnadević et all [23]. Briefly the synthesis consists in following. A deep violet toluene solution of C$_{60}$ (80 mg of C$_{60}$ in 100 ml of toluene) was added dropwise to the aqueous solution of NaOH (2 g in 20 ml of water) containing 10 mg of CTAB and 0.25 ml of H$_2$O$_2$ (30%).

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 at least three times ensuring complete removal of NaOH and CTAB impurities. The precipitate was dried at 60±3 °C for 5 hours. The reaction product was a dark brown solid.
2.2.2. Ultrasonic reactor and its basic properties

The ultrasonication of the reaction mixture was conducted with a thermostatically controlled ultrasonic reactor model VC 750 made by Sonics and Materials Inc. USA. The power of the ultrasonic reactor employed in this research was 750 W and frequency of 20 kHz. The ultrasonic reactor consists of a probe with 13 mm in diameter tip, made of titanium alloy. The temperature was maintained to within ± 1.0 °C by cooling jacket connected to a thermo-cryostat and was monitored using a thermocouple inserted directly into the reaction mixture at the same depth as the probe at app. 0.5 cm distance from the tip. The titanium probe was immersed reproducibly 5 cm below the surface of the reaction mixture. The volume of the reaction mixture was 120 mL.

The ultrasonic power dissipated $P_{\text{diss}}$ (W) in the reaction mixture was determined using the method introduced by Lorimer et al. [24] using the Eq. (1)

$$P_{\text{diss}} = mC_p \left( \frac{dT}{dt} \right)_{\text{res}}$$

where $m$ (g) is solution mass, $C_p$ (J g$^{-1}$ K$^{-1}$) is the specific heat at constant pressure and $dT/dt$ (K s$^{-1}$) is rate of temperature increase. The accumulated power $P_{\text{AC}}$ (W/ml) was calculated by dividing the dissipated power with the volume $V$ (ml) of the reaction mixture.

The ultrasonic intensity $I$ W/cm$^2$ was calculated using the Eq. (2) [25]:

$$I = \frac{P_{\text{diss}}}{V S}$$

where $V$/mL is a volume of the liquid and $S$ is the area of the probe tip (4.17 cm$^2$).

The sonochemical efficiency ($SE$), defined as the ratio of the number of the reacted molecules toward the ultrasound energy, is calculated by Eq. (3) [26]

$$SE = \frac{C \times V}{P_{\text{diss}} \times t}$$

where $C$ (µmol) is the concentration of triiodide formed, $V$ (L) is the solution volume and $t$ (s) is the sonication time.

2.2.3. VIS spectra of the reaction mixture

VIS spectra of both C$_{60}$ solution in toluene and the reaction’s mixtures organic layer were obtained using UV-Visible Spectrophotometer, Cintra 10e, UK.

2.2.4. Elemental analysis of the reaction product

The determination of carbon, oxygen and hydrogen content in the final reaction products at all of the investigated temperatures was performed on a Carlo Erba Elemental Analyzer, type EA 1108, Italy. All of the final products have the same content (C: 63.83 % wt.; O: 34.04 % wt. and H: 2.13 % wt.). Based on the determined chemical composition we can conclude that all the final reaction products had the same formula: C$_{60}$(OH)$_{24}$.

2.2.5. Infrared spectra of the reaction product

The FT-IR spectra of the reaction product samples were recorded in the form of KBr pellets (1 mg of sample to 100 mg KBr) using a Bomem MB100 Fourier transform infrared spectrometer (FT-IR), Hartmann & Braun, Canada.

The FT-IR spectra of the final reaction products at all of the investigated temperatures showed characteristic absorption bands of fullerol: broad band at 3420 cm$^{-1}$ (assigned for νO-H), 1608 cm$^{-1}$ (νC=C), 1400 cm$^{-1}$ (δ$_S$C-O-H) and 1086 cm$^{-1}$ (νC-O) [27-29].
2.3. Methods used to evaluate the kinetic model and kinetic parameters

2.3.1. Model-Fitting Method

According to the model-fitting method, kinetic reaction models of solid state reactions are classified in five groups, depending on the reaction mechanism: (1) power law reaction, (2) phase boundary controlled reaction, (3) reaction order, (4) reaction explained with the Avrami equation, and (5) diffusion controlled reactions. The experimentally determined conversion curve $\alpha_{\text{exp}}=f(t)$ was transformed into the experimentally normalized conversion curve $\alpha_{\text{exp}}=f(t_N)$, where $t_N$ is the normalized time which was determined using Eq. (4):

$$t_N = \frac{t}{t_{0.9}}$$

where, $t_{0.9}$ is the reaction time at $\alpha = 0.9$ [30]. The set of kinetic reaction models used to determine the model of the investigated reaction was undertaken from the work of Vyzovkin and Wight [31]. The kinetic model of the investigated process was determined by analytically comparing the normalized experimental conversion curves with the normalized model’s conversion curves. The kinetics model of the fullerol formation reaction corresponds to the one for which the sum of squares of the deviation of its normalized conversional curve gives minimal values from the experimental normalized conversional curve.

2.3.2. Isoconversion method

The activation energy of the investigated fullerol formation reaction under conventional heating and under ultrasonic field was established using the Friedman method [32] which is based on the rate equation.

$$\frac{d\alpha}{dt} = k(T) \cdot f(\alpha)$$

where $d\alpha/dt$ is the reaction rate, $\alpha$ is the degree of polyhydroxylation, $k(T)$ - the rate constant, $t$ - the time, $T$ - the temperature, and $f(\alpha)$ is the reaction model associated with a certain reaction mechanism. The dependence of the rate constant on the temperature is ordinarily described by the Arrhenius law:

$$-\frac{E_a}{RT} = \ln(A)$$

where $E_a$ is the activation energy, $A$ - the pre-exponential factor and $R$ - the gas constant. Combining Eq. (5) and Eq. (6) we get the following Equation:

$$\ln\left(\frac{d\alpha}{dt}\right)_{\alpha_i} = \ln(A_{\alpha_i} f(\alpha_i)) - \frac{E_{a_i}}{RT_{\alpha_i}}$$

Considering that the reaction rate constant is only a function of the temperature, which is known as the isoconversional principle of Friedman, Eq. (7) is easily transformed into:

$$\ln\left(\frac{d\alpha}{dt}\right)_{\alpha_i} = \ln\left[A_{\alpha_i} f(\alpha_i)\right] - \frac{E_{a_i}}{RT_{\alpha_i}}$$

Where $E_{a_i}$ and $A_{\alpha_i}$ are the activation energy and pre-exponential factor for particular degree of polyhydroxylation

That allows the evaluation of the activation energy for the particular degree of polyhydroxylation. For $\alpha = \alpha_i = \text{const}$, the plot $\ln\left(\frac{d\alpha}{dt}\right)_{\alpha_i}$ vs. $(1/T)_{\alpha_i}$, obtained from conversion curve, should be a straight line whose slope is used to calculate the apparent activation energy [33].
2.4. Determination of degree of fullerene polyhydroxylation ($\alpha$)

During the reaction of fullerene polyhydroxylation the intense colour of the C$_{60}$ toluene solution reduces due to the decrease of concentration in the reaction mixture. The degree of fullerene polyhydroxylation at time (t) can be calculated using Eq. (9):

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

where $C_0$ is the starting concentration of C$_{60}$ in the toluene solution and $C_i$ is the concentration of C$_{60}$ in the organic layer of the reaction mixture at a definite reaction time. The concentration of C$_{60}$ was determined by measuring the absorption at $\lambda = 538$ nm.

3. Results and Discussion

Fig. 1 shows the change in VIS spectra of the organic phase of the reaction mixture obtained during fullerene polyhydroxylation under ultrasonic field at 293 K.

![Vis spectra of organic phase](image)

**Fig. 1.** Change in VIS spectra during fullerol formation under ultrasonic field at 293K.

From the VIS spectra obtained during C$_{60}$ polyhydroxylation it can be seen that the intensity of the absorption peaks at $\lambda_1 = 535$ nm and $\lambda_2 = 592$ nm, which are proportional to the concentration of fullerene in the organic phase, decreases and at the very end of reaction completely disappeared.

Fig. 2 shows the change of C$_{60}$ concentration with time.

The dependence of C$_{60}$ concentration vs. time at different temperatures have similar forms. The curves clearly distinguished three characteristic forms of decreasing C$_{60}$ concentration with time: a linear, a concave and a plateau. Using the data of decreasing C$_{60}$ concentration in the toluene solution and applying Eq. (9) we can calculate the degree of C$_{60}$ polyhydroxylation.
Conversion kinetics curves of the isothermal $C_{60}$ polyhydroxylation under ultrasonic field (isothermal dependence of $\alpha$ on time) are shown in Fig. 3.

Fig. 2. The change of fullerene $C_{60}$ concentration with time.

Fig. 3. Isothermal conversion kinetics curves of $C_{60}$ polyhydroxylation under ultrasonic field.

The isothermal conversion kinetics curves have similar forms at all of the investigated temperatures. The curves clearly distinguished three characteristic forms of increasing $\alpha$ with time: a linear, a convex and a plateau. At the beginning of the $C_{60}$ polyhydroxylation reaction $\alpha$ linearly increase with time, after that the growth of $\alpha$ with time slows down, and at last the process finishes by reaching the plateau value.

With the increase in the reaction’s mixture temperature the duration of the linear increase of $\alpha$ with time and the time required to attend the plateau decreases, which indicate that the rate of $C_{60}$ polyhydroxylation increases with the increase in temperature.

Knowing that the variation of $E_{\alpha}$ with $\alpha$ is a good indicator of a multi-step process,
we applied the Friedman’s isoconversional method to determine the form of the dependence of activation energy on $\alpha$. The dependence of $E_{a,\alpha}$ on the $\alpha$ is presented in Fig 4.

Fig. 4. The dependence of $E_{a,\alpha}$ on the degree of C$_{60}$ polyhydroxylation.

Based on the results shown on Fig. 4 it is easy to conclude that the value of $E_{a,\alpha}$ is independent on the values of the degree of C$_{60}$ polyhydroxylation. The independence of $E_{a,\alpha}$ on $\alpha$, which is in agreement with the principle of Vyazovkin [31], confirms that the C$_{60}$ polyhydroxylation under ultrasonic field is a kinetically elementary reaction which takes place in one step.

Applying the „model fitting“ method it was found with great assurance that model of first order chemical reaction (F1) would be the best model to describe the kinetics of C$_{60}$ polyhydroxylation at all the investigated temperatures. The F1 model is presented with the following equation:

$$\ln(1-\alpha) = k_M \cdot t$$

where, $k_M$ is a model constant for the first-order chemical reaction rate. The dependence of $\ln(1-\alpha)$ on time at all of the investigated temperatures gave straight lines. From the slopes of these linear dependences, the model’s reaction rate constants ($k_M$) were determined.

The influence of temperature on $k_M$ for C$_{60}$ polyhydroxylation under conditions of conventional heating and under ultrasonic field is shown in Tab. 1. Since the temperature dependence of the model kinetics constant for the reaction rate was expressed by the Arrhenius equation, the kinetics model’s parameters (model activation energy and pre-exponential factor) of C$_{60}$ polyhydroxylation were determined. The obtained results are also given in Tab. I.

Tab. I The influence of temperature on the model’s rate constant and kinetic parameters

<table>
<thead>
<tr>
<th>T [K]</th>
<th>Conventional heating</th>
<th>Ultrasonic field</th>
<th>Kinetic parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$k_M^{CH}$ [min$^{-1}$]</td>
<td>$k_M^{US}$ [min$^{-1}$]</td>
<td>$E^{CH}$ [kJ/mol]</td>
</tr>
<tr>
<td>293</td>
<td>0.05</td>
<td>0.10</td>
<td>40±1</td>
</tr>
<tr>
<td>303</td>
<td>0.08</td>
<td>0.18</td>
<td></td>
</tr>
<tr>
<td>313</td>
<td>0.14</td>
<td>0.21</td>
<td></td>
</tr>
</tbody>
</table>
If we compare the results obtained from the investigation of the isothermal kinetics of C\textsubscript{60} polyhydroxylation under ultrasonic field with the kinetics data obtained under the conditions of conventional heating [23] the reaction mixture, one can conclude the followings:

a) The isothermal C\textsubscript{60} polyhydroxylation rate is from 1.5 times to 2.2 times higher;

b) The application of ultrasonic field does not influence the kinetics model of C\textsubscript{60} polyhydroxylation reaction;

c) The activation energy for the reaction of active complex formation under ultrasonic field is about 28% lower, whereas a pre-exponential factor value is 40 times higher than the corresponding values under the conventional heating;

d) There is a linear relationship between \( E_a \) and \( \ln A \) of C\textsubscript{60} polyhydroxylation, under ultrasonic field and under conventional heating, which implies on the compensation effect of type 2.

Ultrasound is known to manifest physical and chemical effect on heterogeneous reaction system through cavitation bubbles as follows: a) the physical effect of emulsification, in which the micro turbulence generated due to radical motion of bubbles, creates intimate mixing of the immiscible reactants. Due to this, the interfacial area between the reactants. Increases enormously, giving faster reaction kinetics; b) the chemical effect, in which radicals (such as \( \cdot OH \), \( \cdot CH \)) are produced during transient collapse of the bubble that induce/accelerate chemical reaction in the bulk medium.

Tab. II shows the values for the basic characteristics of the applied ultrasonic reactor: dissipation power (\( P_{disp} \)), specific absorbed acoustic power (\( P_{ac} \)), ultrasonic intensity (\( I \)), and sonochemical efficiency (\( SE \)).

<table>
<thead>
<tr>
<th>Characteristic</th>
<th>Unit</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>( P_{disp} )</td>
<td>W</td>
<td>6.41</td>
</tr>
<tr>
<td>( P_{ac} )</td>
<td>W/ml</td>
<td>0.05</td>
</tr>
<tr>
<td>( I )</td>
<td>W/cm\textsuperscript{2}</td>
<td>8.16</td>
</tr>
<tr>
<td>( SE )</td>
<td>( \mu \text{mol}/J )</td>
<td>( 3*10^{-5} )</td>
</tr>
<tr>
<td>Frequency</td>
<td>kHz</td>
<td>20</td>
</tr>
<tr>
<td>Amplitude</td>
<td>%</td>
<td>30</td>
</tr>
</tbody>
</table>

The increase of chemical reaction rate under ultrasonic field is usually attributed to the existence of hot spots. [34]

The above established facts represent a reliable basis to establish the objective influence of ultrasound field on kinetics of C\textsubscript{60} polyhydroxylation. Since, the dependences of \( k_M \) vs. temperature under conventional heating and under ultrasound field obeys the Arrhenius equation, we can claim that:

\[
\left( \frac{k_{MUS}}{k_{MC}} \right) = \frac{A_{US}}{A_C} \exp \left( \frac{E_{US}^{CH} - E_{US}^{PS}}{RT} \right)
\]

where: \( k_{MUS} \) is model’s rate constant of C\textsubscript{60} polyhydroxylation under ultrasonic field, \( A_{US} \) and \( E_{US}^{CH} \) are pre-exponential factor and activation energy of reaction under ultrasonic field. In case when \( E_{US}^{CH} = E_{US}^{PS} \) the Eq. (11) is transformed to:
The above expression clearly indicates that the increase in the reaction rate under ultrasound field is not influenced by temperature, but it is directly proportional to the increased value of the pre-exponential factor.

\[
\left( \frac{k_{US}}{k_{CH}} \right) = \frac{A_{US}}{A_{CH}}
\]  
\( (12) \)

The influence of temperature on \( \left( \frac{k_{US}}{k_{CH}} \right) \) is shown in Tab. III.

<table>
<thead>
<tr>
<th>( T ) [K]</th>
<th>( \left( \frac{k_{US}}{k_{CH}} \right) )</th>
<th>1680</th>
<th>305</th>
<th>12</th>
</tr>
</thead>
<tbody>
<tr>
<td>293</td>
<td>2.00</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>303</td>
<td>2.25</td>
<td>2039</td>
<td>320</td>
<td>17</td>
</tr>
<tr>
<td>313</td>
<td>1.50</td>
<td>1024</td>
<td>321</td>
<td>8</td>
</tr>
</tbody>
</table>

As it can be seen from the results shown in Tab. 3, the values of \( \left( \frac{k_{US}}{k_{CH}} \right) \) change complexly with the increase in temperature and they are significantly lower than the values, which indicates that ultrasound field have influence on the values of activation energy. In case when \( A_{US} = A_{CH} \), the Eq. (11) is transformed to:

\[
RT \ln \left( \frac{k_{US}}{k_{CH}} \right) = \Delta E_{US} - E_{CH}
\]  
\( (13) \)

Then, the value of term \( RT \ln \left( \frac{k_{US}}{k_{CH}} \right) \) is independent on temperature and equals \( \Delta E_{US} - E_{CH} \). Also, as it can be seen from the results presented in Tab. III the values of the term \( RT \ln \left( \frac{k_{US}}{k_{CH}} \right) \) change complexly with temperature and it is significantly lower than the difference between the activation energies \( \Delta E_{US} - E_{CH} \) which, once again, indicates that ultrasonic field have influence on pre-exponential factor.

In the case when \( E_{CH} = E_{US} \) and \( A_{US} = A_{CH} \) the Eq. (14) enables to calculate the actual temperature \( T_{US} \) for reaction mixture under ultrasonic field, that corresponds to the experimentally calculated value of the rate constant.

\[
T_{US} = \frac{E_{CH}}{R \left[ \ln \left( \frac{k_{US}}{k_{CH}} \right) \right]}
\]  
\( (14) \)

The values of \( T_{US} \) complexly change with temperature which points out that ultrasonic field have influence on the values of \( E_{CH} \) and \( A \).

The calculated values of \( \Delta T \) significantly exceeds the accuracy of measured temperature in the reaction system (± 1 K) which approves that temperature increase in the reaction system is not a consequence of reaction rate increase in the ultrasonic field.
The established decrease in the values of $E_a$ and $\ln A$ of fullerene polyhydroxylation under ultrasonic field compared to the conventional heating permits the possibility of new explanation of the influence of ultrasonic field on the kinetics of isothermal fullerene polyhydroxylation based on integration of Larsson model of activating the molecule via selective energy transfer (SET model) [35]. The basic assumptions of the SET model are: a) there is the possibility of coupling between vibration modes of the fullerene molecule ($\nu$) and vibration modes ($\omega$) of the reaction mixture; b) the activated complex for the fullerene polyhydroxylation is formed via the resonant (selective) transfer of required energy from the reaction mixture to resonant vibration mode of fullerene molecule; c) the value of transferred energy is quantized and it is determined by the number of resonant vibration quanta ($n$) which are exchanged between the reaction environment and the resonant vibration mode of fullerene molecule; d) resonant transfer of energy causes the change in the value of anharmonicity factor of the resonant vibration mode.

Based on the assumptions above, in accordance with the SET model, considering this resonance system as a classical forced damped harmonic oscillator, it is possible to get the expression for reaction rate constant and isokinetic temperature ($T_{ic}$).

$$lnk = \ln A + \frac{\omega}{\nu^2 - \omega^2} \left[ \frac{\nu}{2} - \frac{\nu \omega}{2(\nu^2 - \omega^2)} \right] \sum \Delta E_i \frac{2}{\hbar c} - \frac{E_a}{RT}$$

(15)

where $\Delta E_i = \hbar c \nu_i$ is the energy increment between the two levels $n_i$ and $n_{i+1}$, $\hbar$ is the Planck constant and $c$ is the velocity of light.

As $\sum \Delta E_i = E_a$, Eq. (15) can be rewritten in the following form:

$$lnk = \ln A + \frac{E_a}{R} \left( \frac{1}{T_{ic}} \right)$$

(16)

where the $T_{ic}$ is the isokinetic temperature:

$$T_{ic} = \frac{N\hbar c \nu^2 - \omega^2}{\nu \omega} \frac{1}{\frac{\frac{\nu}{2} - \frac{\nu \omega}{2(\nu^2 - \omega^2)}}{\hbar c}}$$

(17)

For resonance conditions, Eq. (17) can be transformed to:

$$T_{ic} = \frac{Nhcv}{2R} = 0.715\nu$$

(18)

where $\nu$ is given in cm$^{-1}$ and $T_{ic}$ is in K degrees.

The isokinetic temperature is in a relationship with the equation of compensation effect by the expression:

$$T_{ic} = \frac{1}{b}$$

(19)

where $b$ is the slope of the equation of compensation effect. The equation of compensation effect is given with the expression:

$$\ln A = a + b \cdot E_a$$

(20)

where $a$ is the parameter of compensation equation.

In the case of the existence of compensation equation which connects the values of the kinetic parameters ($E_a$ and $\ln A$) calculated under different experimental conditions (conventional heating and ultrasound field) it is possible to calculate the values for the $T_{ic}$ and the $\nu$, based on the known value of the $b$. There is a functional relationship between the calculated values of the kinetic parameters of fullerene polyhydroxylation under the conventional heating and under ultrasonic field which is expressed as:

$$\ln A = 0.336 + 0.354 \cdot E_a$$

(21)

where $E_a$ and $\ln A$ are the activation energy and pre-exponential factor in a defined experimental conditions (conventional heating and ultrasound field).
In accordance with Larson’s model the value of activation energy is given by the expression:

\[ E_a - RT = n\nu(1 + nx) \]  \hspace{1cm} (22)

where \( x \) is anharmonicity factor and \( n \) is the integer vibration quantum number. Based on the known values of the \( E_a \) and \( \nu \) the values of \( n \) and \( x \) are calculated as follows:

\[ n = \frac{E_a - RT}{\nu} \]  \hspace{1cm} (23)

\[ x = \frac{(E_a - RT)/n - 1}{n} \]  \hspace{1cm} (24)

The values of \( \nu \), \( n \) and \( x \) for fullerene polyhydroxylation under ultrasonic field and conventional heating are given in Tab. IV.

**Tab. IV** The values of \( \nu \), \( n \) and \( x \) for fullerene polyhydroxylation under ultrasonic field and conventional heating

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Conventional heating</th>
<th>Ultrasonic field</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \nu ), cm(^{-1} )</td>
<td>500</td>
<td>500</td>
</tr>
<tr>
<td>( n )</td>
<td>7</td>
<td>2</td>
</tr>
<tr>
<td>( x )</td>
<td>-0.023</td>
<td>-0.015</td>
</tr>
</tbody>
</table>

From the results given in Tab. IV, it could be concluded that ultrasonic field does not lead to the changes in the mechanism of activation of fullerene molecules for polyhydroxylation. Both in the case of ultrasonic field and conventional heating the mechanism of activation is identical and goes via resonant transfer of required energy \( (E_a) \) from the reaction environment (out-of-plane bending C-C-C vibration of toluene molecules) to the resonant vibration mode of fullerene molecule which have the value of wave number = 500 cm\(^{-1} \), which corresponds to \( A_g(1) \) vibrational mode of \( C_{60} \) molecule.

Therefore, the lower value of \( E_a^{PS} \) and \( E_a^{CH} \) is a consequence of less number of necessary quanta \((n=2)\) required to activate the \( C_{60} \) molecule under ultrasonic field compared to the number of quanta in conditions of conventional heating \((n=7)\). The decrease in the number of necessary quanta is most probably due to the increase of the ground resonant vibrational mode of \( C_{60} \) and toluene molecules, which is caused with absorption of the energy of ultrasonic field. The lower value of \( lnA \), which is in agreement with decreased value of \( E_a \), is explained with lower number of configuration, which is confirmed with the higher values of anharmonicity factor [36, 37].

4. Conclusion

The reaction of isothermal \( C_{60} \) polyhydroxylation under ultrasonic field is a kinetically elementary reaction (one-step reaction) that is described by the kinetics model of first-order reaction.

The conditions of ultrasonic field actions leads to the decrease in the values of kinetics parameters \((E_a, lnA)\) in comparison to their values obtained under the conventional heating.

The increase in the isothermal rate of \( C_{60} \) polyhydroxylation under ultrasonic field is not a consequence of the increasing temperature in the reaction system, but is caused with the specific influence of the ultrasonic field on the oscillators of fullerene \( C_{60} \) molecules.
The activation of C\textsubscript{60} molecule happens by selective transfer of certain number of resonant quanta from toluene molecules (out-of-plane bending C-C-C vibration) onto the resonant vibrational mode of C\textsubscript{60} molecule (\(\nu = 500 \text{ cm}^{-1}\), which corresponds to \(A_g(1)\) vibrational mode of C\textsubscript{60} molecule).

The activation energy is quantized value and it is determined with the number of resonant quanta that are transferred.

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5. References


**Садржај:** Испитана је изотермна кинетика полихидроксилације фулерена под утицајем ултразвучног поља. Одређене су изотермне кинетичке криве полихидроксилације фулерена на различитим температурама у опсегу од 293 K до 313 K. Применом изоконверзионе методе устанољено је да је реакција полихидроксилације фулерена са натријумхидроксидом и цетилтриметиламонијумброму вом, као фазног катализатора, кинетички елементарна реакција.
Методом укључивања у реакциони модел је потврђено да кинетички модел реакције првог реда најбоље описује кинетику полихидроксилације фулерена под утицајем ултразвучног поља, и одређени су кинетички параметри полихидроксилације фулерена ($E_a = 29 \text{ kJ/mol and } \ln A = 9.4 \text{ min}^{-1}$).
Устанољено је да је брзина реакције полихидроксилације фулерена под утицајем ултразвучног поља од 1,5 до 2,2 пута већа од брзине те реакције при конвенционалном загревању реакције смеси. Активациона енергија је 28% мања у односу на активацију енергију одређену при конвенционалном загревању, док је вредност предекспоненцијалног фактора 40 пута већа.
Ниже вредности активације енергије ($E_a$) и предекспоненцијалног фактора ($\ln A$) под утицајем ултразвучног поља објашњене су повећањем основног енергетског нивоа резонантног вибрационог мода ($v = 500 \text{ cm}^{-1}$) молекула фулерена ($A_g(1)$ вибрациони мод) и молекула толуена („out-of plane“ савијајућа C-C-C вибрација), и смањењем вредносњу фактора аномармоничности.
**Кључне речи:** Полихидроксилација фулерена, кинетика, ултразвучно поље