Kinetics of Iodine-catalyzed Conjugation of Soybean Oils

Jie Yan1*, Huimin Huang1, Jinlan Yang1, Qiqi Zhan2, Chunyuan Tan2, Hailin Lin1 and Guojie Wu1

1College of Chemistry and Chemical Engineering, Zhongkai University of Agriculture and Engineering, Guangdong 510225, China
2College of Light Industry and Food Science, Zhongkai University of Agriculture and Engineering, Guangdong 510225, China
*Corresponding author’s e-mail: yanjie0001@126.com

Abstract. Kinetics of iodine-catalyzed conjugation of soybean oils was studied. The results indicated that the conjugation of linoleic acid could be described by means of apparent first-order reaction. The apparent activation energy values and the preexponential factor A were 769kJ/mol and 3.49×108 s⁻¹, respectively. The rate equation was  \( r_A = \frac{dC_{LA}}{dt} = -3.49 \times 10^8 \exp\left[\frac{9249.88}{T}\right]C_{LA}C_{I_1}^{0.9425} \). It was also clear that the model was perfect for fitting the results.

1. Introduction

Oil conjugation, as a method of oil modification, has attracted much attention recently. Alkali isomerization is the most widely used method for conjugation in industry at present. The method needs a large amount of acid, alkali, high boiling point organic solvent and washing water. The shortcomings of complex procedures, difficult to guarantee the quality of final product, high energy consumption and serious environmental pollution are inevitable. To solve these problems, many researchers are searching for new catalysts and attempting to conjugate oils using environmentally friendly approaches.

Iodine is inexpensive and non-toxic, and it has been reported that iodine can catalyze a variety of organic reactions[1-7]. There have also been reports concerning the conjugation of oils using iodine as a catalyst. Gangidi[8] prepared conjugated linoleic acid (CLA) using iodine as a catalyst within a temperature range of 35-40°C and irradiation with a mercury lamp for 120h, but the yield of CLA was not high. The conjugation of fatty acid methyl esters using iodine as a catalyst has also been investigated by preparing methyl esters, reacting at high temperature in the presence of iodine, and then vacuum distilling to obtain the final product [9-10]. However, the preparation of fatty acid methyl esters is complicated and serious environmental pollution. For these reasons, a new method of iodine-catalyzed conjugation of oil was carried out in our former study. The method, using transgenic soybean oil without methyl esterification as the raw material, has characteristics of short procedure, environmentally friendly, easy operation and high conversion rate. To clarify the fundamental basis for expanding test and large-scale production, the main purpose of this work is to clarify the effects of reaction time, temperature and catalyst amount et.al on reaction rate and establish a kinetic equation.
2. Materials and methods

2.1 Materials and instrumentation
Transgenic soybean oil was purchased from Cofco Corporation. The mass fraction of linoleic acid (LA) and linolenic acid (LNA) determined by GC was 50.88% and 6.86%, respectively. Analytical-grade iodine was purchased from Tianjin Zhongxing Chemical Reagent Factory. The standard products of conjugated linoleic acid (CLA, >99% purity) were purchased from Nu-Chek-Prep Inc., Nitrogen (99.99% purity) was obtained from Guangzhou Chun Jiang Industrial Gas Co., Ltd. All other chemical reagents were analytical grade.

The following instrumentation was used for sample preparation and analysis: UV spectrophotometer (2550, Shimadzu, Japan); magnetic agitator with heat collection and temperature control (DF-101S, Gongyi Yingyu Instrument Factory, China).

2.2 Methods

2.2.1 Preparation of conjugated oil
A certain amount of oil and iodine was placed in a three-necked flask and was heated and stirred under the protection of high-purity nitrogen. The system was refluxed at a given temperature for a period of time, then was cooled to room temperature and washed 3 times with sodium hyposulfite solution and distilled water to remove the iodine. Then, the sample was obtained after drying with anhydrous sodium sulfate.

2.2.2 Measurement of the CLA concentration
Standard solutions were prepared by accurately weighing the CLA standard and dissolving it with n-hexane in volumetric flasks to prepare a series of standard solutions that ranged from 4mg/L to 14mg/L in concentration. Using n-hexane as the reference solvent, the absorbance of each solution at a wavelength of 234nm was measured and plotted against its corresponding concentration. A linear regression analysis was performed, yielding the equation $A=0.1047C-0.046$, where $A$ is the absorbance and $C$ is the molar concentration of CLA (μg/mL). The $R^2$ value was equal to 0.9992.

The concentration of CLA in the product was determined by weighing the samples and transferring them to volumetric flasks. The samples were diluted to the scale mark with n-hexane. The CLA concentrations were then determined by measuring the absorbances and using the standard solution linear regression to calculate the CLA concentrations.

2.2.3 Experimental scheme

| Table1 Experiment design for kinetics | temperature / ℃ | molar concentration of catalyst / (mol/L) |
| --- | --- | --- |
| test No. | 180 | 0.0183 |
| 1 | 180 | 0.0229 |
| 2 | 180 | 0.0298 |
| 3 | 170 | 0.0298 |
| 4 | 160 | 0.0298 |
| 5 |

| Table2 Apparent first-order rate constants | reaction rate ka / min⁻¹ | $R^2$ |
| --- | --- | --- |
| test No. | 0.84×10⁻² | 0.9993 |
| 1 | 1.00×10⁻² | 0.9997 |
| 2 | 1.31×10⁻² | 0.9995 |
| 3 | 0.78×10⁻² | 0.9968 |
| 4 | 0.51×10⁻² | 0.9992 |
| 5 |
3. Results and discussion

3.1 Establishment of dynamics model
Iodine-catalyzed conjugation of oils is homogeneous. LA and LNA will be conjugated in the reaction. As the amount of LA is far more than that of LNA, from simple, convenient and practical point of view, the dynamics model was established only considering the conjugation of LA, ignoring the existence of LNA in the system.

Reaction equation is
\[
\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH} \rightarrow \text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}.
\]

It is abbreviated as \( \text{LA} \rightarrow \text{CLA} \). Taking the effect of catalyst on reaction rate into account, the kinetic equation is
\[
\frac{dC_{LA}}{dt} = k_0 C_{LA}^{\alpha} C_{I_2}^{\beta} \quad (1)
\]

Where, \( r_A \) is reaction rate; \( k_0 \) is rate constant; \( C_{LA} \) is concentration of LA at \( t \) moment, mol/L; \( C_{I_2} \) is concentration of catalyst, mol/L; \( \alpha, \beta \) are impact index of initial concentration of LA and catalyst, respectively.

According to equation (1), when temperature and catalyst concentration invariable, the following equation can be got: \( r_A = k_a C_{LA}^{\alpha} \quad (2) \)

\[ k_a = k_0 C_{I_2}^{\beta} \quad (3) \]

Integral the former (2) and get,
\[
\frac{1}{a-1} \frac{C_{LA}^{a-1}}{C_{LA0}^{a-1}} = (a-1)k_a t, a \neq 1, \quad (4)
\]

\[
\ln \frac{C_{LA0}}{C_{LA}} = k_a t, a = 1 \quad (5)
\]

Where, \( k_a \) is reaction rate while temperature and catalyst concentration constant; \( k_0 \) is intrinsic rate constant, it is the function of temperature; \( C_{LA0} \) is initial concentration of LA, mol/L; \( C_{LA} \) is instant concentration of LA, mol/L.

3.2 Determination of parameters of the model
During the test, determining the concentration of CLA, then calculate the concentration of LA. Changing of \( \ln(C_{LA0} / C_{LA}) \) with reaction time \( t \) is shown in figure 1.
Fig. 1 Changes of $\ln(C_{La0}/C_{La})$ with reaction time

As can be seen from figure 1, $\ln(C_{La0}/C_{La})$ is roughly linear with reaction time. Therefore, the reaction could be described by means of apparent first-order reaction, $\alpha = 1$. The first-order rate constants of different experiments are shown in table 2.

According to table 2, there are large differences of apparent first-order rate constants of different experiments. At the same temperature, the difference is obvious. It is indicated that the effect of catalyst dosage on reaction rate is significant.

Transform the formula $k_u = k_0 C_{i2}^\beta$ to $Lnk_u = Ln k_0 + \beta Ln C_{i2}$. If temperature is invariant, $Ln k_0$ is constant. The slope of curve $Lnk_u - LnC_{i2}$ is $\beta$, it can be determined from test 1, 2 and 3. As can be seen in figure 2, $\beta = 0.9425$. 

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Table 2

| Experiment | $k_u$ | $R^2$ |
|------------|-------|-------|
| 1          | 0.0051 | 0.9984 |
| 2          | 0.01  | 0.9994 |
| 3          | 0.0131 | 0.9989 |
| 4          | 0.0078 | 0.9936 |
| 5          | 0.0051 | 0.9984 |
Fig. 2 Relationship between $\text{Ln}k_a$ and $\text{Ln}C_{t_2}$

Fig. 3 Relationship between rate constants and temperature

3.3 Reaction activation energy

Arrhenius equation is $k_0 = A \exp\left(-\frac{E_a}{RT}\right)$  \( (6) \)

Where, $k_0$ is rate constant, s$^{-1}$; $A$ is Arrhenius frequency factor, s$^{-1}$; $E_a$ is activation energy, J/mol; $R$ is gas constant, J/(mol·K); $T$ is thermodynamic temperature of reaction, K.

Using logarithm on both sides of formula (6), get: $\text{Ln}k_0 = -\frac{E_a}{RT} + \text{Ln}A$  \( (7) \)

Plotting $\text{Ln}k_0-1/T$, the slope of the curve is -$E_a/R$, and intercept is $\text{Ln}A$.

According to figure 3, the activation energy is $E_a = 9249.88 \times 8.315 = 7.69 \times 10^5$ J/mol, $\text{Ln}A = 19.67$, the pre-exponential factor $A = 3.49 \times 10^8$ (S$^{-1}$). Putting pre-exponential factor and activation energy into formula (6), get:

$$k_0 = 3.49 \times 10^8 \exp\left[-\frac{9249.88}{T}\right]$$  \( (8) \)

Putting formula (8) into formula (1), get the rate equation:

$$r_a = \frac{dC_{CLA}}{dt} = -3.49 \times 10^8 \exp\left[-\frac{9249.88}{T}\right]C_{t_2} C_{LA}^{0.9425}$$  \( (9) \)

Integrate formula (9), get dynamic equation:

$$C_{CLA} = C_{CLA0} - 2.117 \exp[-3.49 \times 10^8 \left(-\frac{9249.88}{T}\right)^{0.9425}C_{t_2}^{0.9425}]$$

3.4 Fitting the model to experimental results
As can be seen from figure 4, in general, the model predicts the experiment results very well.

4. Results
(1) Dynamics of iodine-catalyzed conjugation of oil was studied. The results indicated that the conjugation of LA could be described by means of apparent first-order reaction. The apparent activation energy values and the pre-exponential factor $A$ were $769 \text{kJ/mol}$ and $3.49 \times 10^8 \text{s}^{-1}$, respectively. The rate equation was $r_A = \frac{dC_{CLA}}{dt} = -3.49 \times 10^8 \exp\left[\frac{9249.88}{T}\right]C_{LA}C_{t_1}^{0.9425}$. The dynamic equation was $C_{CLA} = C_{LA0} - 2.117 \exp\left[-3.49 \times 10^8 e^{\frac{9249.88}{T}}C_{t_1}^{0.9425}\right]$. (2) It was also indicated that the model predicts the results very well.

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