KINETICS STUDY ON NITRATION OF METHYL RICINOLEATE

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Received November 7, 2011; Accepted February 7, 2012

ABSTRACT

Kinetics parameter values of methyl ricinoleate nitration (rate constant, reaction order and the rate of reaction) have been determined. Nitration was carried out with both concentrations of HNO₃ and acetic anhydride in excess to the concentration of methyl ricinoleate. Thus, the kinetics parameter value was only affected by the concentration of methyl ricinoleate. Based on kinetic study conducted, it could be concluded that the nitration follows pseudo first-order, and the reaction rate for methyl ricinoleate with initial concentration of 0.375, 0.325 and 0.250 M were 3.736 x 10⁻⁵, 2.471 x 10⁻⁵, and 1.724 x 10⁻⁵ M/s respectively, with the rate constant at 29 °C was 6.667 x 10⁻⁴ (s⁻¹).

Based on evaluation of FTIR spectra could be estimated that the nitration produces compounds containing functional groups of -NO₃ and -NO₂.

Keywords: nitration; methyl ricinoleate; kinetics

INTRODUCTION

Nitration is an important reaction in the industrial world. Products of nitration are widely used in industrial paint, explosives and fuel additives [1]. On nitration raw material is reacted with HNO₃ and H₂SO₄ or acetic anhydride generally [2-3].

Lately, the nitration processes to obtain the additive as a cetane improver on diesel oil are increasingly receiving attention. This is due to the declining quality of crude oil and this impact on the quality of diesel oil which is resulted. One of the nitration compounds that are widely used as an additive is 2-ethylhexyl nitrate (EHN) [4]. This compound is resulted from nitration of propene derivatives at which it was produced from cracking of petroleum and flammable [5]. Therefore, some researchers [5-9] attempt to find another alternative by using triglycerides or fatty acids as raw material. However, although studies on the nitration process of triglycerides or fatty acids and their derivatives have been widely performed, but the study of the kinetics aspect is still very limited.

Determination of kinetics parameter values of a reaction can be performed by conditioning the concentration of one reactant is much larger than the others [10]. This method can also be applied for determination of value of kinetics parameter of nitration, as has been conducted by some researchers [11-13]. Lewis and Moodie [11] reported that the nitration of styrene with the concentration of nitric acid in excess (> 10 fold) is a pseudo first-order. This also occurs in the nitration of methanol [12] and toluene [13]. This paper reports that nitration of methyl ricinoleate is also a pseudo first-order.
EXPERIMENTAL SECTION

Materials

Some materials used in this study were methyl ricinoleate 98.7% (GC), HNO\(_3\) 65% (Merck), anhydride acetic (Merck), diethyl ether (Merck), anhydrous Na\(_2\)SO\(_4\) (Merck), universal pH paper (Merck), and distilled water (Physical Chemistry Laboratory UGM).

Instrumentation

Some of the main instruments used in this study were the three neck distillation flask (Pyrex), the cooler of ball type (Pyrex), magnetic stirrer (Stuart SB 163), water bath, separating funnel (Pyrex), and gas chromatography (GC Hawlett Pacard 5890 seri II).

Procedure

**Mol ratio of HNO\(_3\) to methyl ricinoleate (MR) determination**

The experiment was intended to determine the optimum mole ratio of HNO\(_3\) on methyl ricinoleate. The optimum mole ratio can be determined from the concentration of residual of MR which was observed in the reaction mixture by gas chromatography (GC). The nitration was carried out at room temperature with reaction time of 25 min. Here the number of moles of each reactant and the mole ratio of HNO\(_3\) and MR were used in this experiment.

**Methyl ricinoleate nitration**

In the nitration process, initially HNO\(_3\) was added in the flask, and then followed by addition of acetic anhydride. Furthermore, a magnetic stirrer was operated slowly (200 rpm), until the temperature in the distillation flask becomes constant. After the temperature constant, then methyl ricinoleate was added into a flask quickly. After the reaction run for t min, the sample was taken for purification process.

Purification was carried out by adding the sample in 200 mL of ice water, and then the mixture was put in a separating funnel (500 mL), and followed by addition of diethyl ether (20 mL). Furthermore, the upper layer was washed using 50 mL of distilled water several times until the washing water become neutral. The upper layer was dried with anhydrous Na\(_2\)SO\(_4\), and then allowed to stand for 24 h. The mixture was filtered and the diethyl ether layer was evaporated by heating at a temperature of 80 °C for about 30 min. Evaporation was stopped after a constant weight was obtained, then analyzed by GC and FTIR.

| Table 1. Mole ratio of HNO\(_3\) to methylricinoleate (MR) |
|----------------|----------------|----------------|
| Reactant        | HNO\(_3\) (mole; mL) | MR (mole; mL) | Mole ratio (HNO\(_3\):MR) |
| No.             | 0.010; 0.7       | 0.010; 3.3     | 1:1                        |
| 2.             | 0.020; 1.4       | 0.004; 1.3     | 5:1                        |
| 3.             | 0.040; 2.8       | 0.004; 1.3     | 10:1                       |
| 4.             | 0.045; 3.0       | 0.003; 1.0     | 15:1                       |
| 5.             | 0.040; 2.8       | 0.002; 0.6     | 20:1                       |
| 6.             | 0.100; 7.0       | 0.004; 1.3     | 25:1                       |

| Table 2. Variation of mole and volume of MR, AA and HNO\(_3\)|
|----------------|----------------|----------------|
| HNO\(_3\) (mole; mL) | AA (mole; mL) | MR (mole; mL) |
| 0.270; 18       | 0.270; 24     | 0.018; 6       |
| 0.270; 18       | 0.270; 24     | 0.015; 5       |
| 0.270; 18       | 0.270; 24     | 0.012; 4       |

Note: Total volume of reactant was 48 mL. Control of total volume was carried out with H\(_2\)O addition.

**Determination of kinetics parameter values of methyl ricinoleate nitration**

Determination of kinetics parameter values was performed by varying the number of moles of methyl ricinoleate (MR), while the number of moles both HNO\(_3\) and acetic anhydride (AA) were not varied. The nitration was conducted at room temperature with the variation of reaction time (5, 11, 17, 23 and 29 min).

RESULT AND DISCUSSION

**The optimum mole ratio of HNO\(_3\) to MR**

HNO\(_3\) is a polar compound, and methyl ricinoleate (MR) has a relatively low polarity. Therefore HNO\(_3\) and methyl ricinoleate can not mix well in any ratio. While this reaction required a high homogeneity of mixture, so the reaction can be run optimally. Therefore, it was necessary to vary the ratio of moles of HNO\(_3\) to the acetic anhydride. The optimum mole ratio was observed from the low concentration of the residual MR determined by GC. Fig. 1 showed the relationship of concentration of residual MR to different mole ratio. Based on Fig. 1 could be shown that the optimum mole ratio was at range 15:1 to 20:1. Therefore, the nitration then was performed on those ratios. For the area ratio of 1:1, 5:1 and 10:1, the concentrations of residual methyl ricinoleate in the reaction mixture were still high. This was caused by a mixed system that had not been homogeneity. As for the ratio of 25:1 was caused by low concentrations of methyl ricinoleate in the mixture.
Nitration of methyl ricinoleate and the results of GC and FTIR analysis

Firstly, nitration was performed by mixing of HNO₃ with acetic anhydride. The mixing was intended to get the nitronium ion (NO₂⁺) that act as electrophiles. Nitronium ion was formed as a result of interaction between HNO₃ with acetic anhydride through the following mechanisms.

\[
\text{CH}_3\text{CO}_2\text{H} + \text{HNO}_3 \rightarrow \text{CH}_3\text{CO}_2\text{H} + \text{NO}_2^+ + \text{H}_2\text{O}
\]

On the nitration process, nitronium ion reacted with methyl ricinoleate to form a new compound. Observation on the new compound was performed by gas chromatography (GC). Fig. 2 showed chromatograms of methyl ricinoleate before nitration (a) and after nitration (b).

### Table 3. Interpretation of bonds and functional groups of the methyl ricinoleate

<table>
<thead>
<tr>
<th>No.</th>
<th>Wavenumber (1/cm)</th>
<th>Bond (kind of vibration)</th>
<th>Functional group</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>3421.78</td>
<td>O-H (stretching)</td>
<td>Alcohol</td>
</tr>
<tr>
<td></td>
<td>1246.04</td>
<td>C-O (stretching)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>3009.00</td>
<td>C-H (stretching)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>856.41</td>
<td>C-H (bending)</td>
<td>Alkene</td>
</tr>
<tr>
<td>2.</td>
<td>2927.99</td>
<td>C-H (stretching, antisymmetric)</td>
<td>Alkyl</td>
</tr>
<tr>
<td></td>
<td>2854.70</td>
<td>C-H (stretching, symmetric)</td>
<td>Alkyl</td>
</tr>
<tr>
<td></td>
<td>1462.07; 1438.92</td>
<td>C-CH₃ (stretching)</td>
<td>Methylene</td>
</tr>
<tr>
<td></td>
<td>1361.77</td>
<td>-CH₃ (stretching)</td>
<td>Methyl</td>
</tr>
<tr>
<td></td>
<td>725.25</td>
<td>C-H (stretching)</td>
<td>Long chain alkyl</td>
</tr>
<tr>
<td>3.</td>
<td>1739.82</td>
<td>C=O (stretching)</td>
<td>Ester</td>
</tr>
<tr>
<td>4.</td>
<td>1199.74 and 1172.74</td>
<td>C-O (stretching)</td>
<td>Ether</td>
</tr>
<tr>
<td>5.</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
According to Suppes et al. [5], the formation of nitrate and nitro groups was characterized by the wavenumber spectrum at 1553 and 1375 cm\(^{-1}\). Based on this information, it could be estimated that the compound which was resulted from nitration of methyl ricinoleate was a molecule containing nitrate and nitro groups.

### The rate constant, the reaction order and the rate of reaction

According to House [16], on the reaction of \(A + B + C \rightarrow \text{Product}\), at which \([A]\) and \([B]\) were set such that both were excess to \([C]\), then \([A]\) and \([B]\) will not change significantly to change in \([C]\). Therefore, the change of \([MR]\) to the initial concentration \([\text{[MR]}_0]\) could be expressed as:

\[
\frac{dx}{dt} = k \left[ \text{HNO}_3 \right]^q \left[ \text{[AA]} \right]^v (\text{[MR]}_0 - x)^w
\]

Later in the determination of the reaction order \((q)\), if the reaction order equal to 1, then through the relationship \(d \text{[MR]} / \text{[MR]} = - k \, dt\), by integrating the equation would be obtained:

\[
\text{ln \, [MR]} = \text{ln \, [MR]}_0 - \text{kt}
\]

From equation 3, then by plotting \(\text{ln \, [MR]}\) versus \(t\) would be obtained a straight line, at which slope equal to \(-k\) for each series of experiment.

Table 4 showed the concentration of residual methyl ricinoleate \([\text{[MR]}]\) in the mixture after reacted for \(t\) min, where the concentration of MR data was obtained by GC. Percentage values in the GC data was multiplied by \([\text{[MR]}]_0\), so that \([\text{[MR]}]\) after the reaction could be determined. Furthermore, the data \([\text{[MR]}]\) was converted into \(\text{ln \, [MR]}\), then used in the plotting of the graph in Fig. 4.

Fig. 4 showed that the resulting line had a high linearity. This was evidenced by the value of \(R^2\) almost close to 1. Thus the initial assumption by assigning values to the MR order reaction equal to 1 was correct. In this case the reaction order of MR was said to be pseudo first order. Then from the equation of the line in Fig. 4 could be seen that the slope was also the value of \(-k\) (average) was equal \(4 \times 10^{-3}\), so that the rate constant value \((k)\) was equal to \(4 \times 10^{-3}\) (min\(^{-1}\)) or equal to \(6.667 \times 10^{-4}\) (s\(^{-1}\)).

On series different initial concentrations, the change concentration of MR with time of reaction were monitored. So by plotting \([\text{[MR]}]\) versus time a reaction rate was evaluated from slope. The slope was obtained by drawing a tangent curve starting from \(t = 0\).
Based on Fig. 5, and then carried out the calculation as follows:

\[
\text{Rate}_{\text{series 1}} = \frac{(0.310 - 0.375)}{(29 - 0)} = -0.00224138 \text{ M/min} = -3.736 \times 10^{-5} \text{ M/s}
\]

\[
\text{Rate}_{\text{series 2}} = \frac{(0.270 - 0.312)}{(29 - 0)} = -0.00148276 \text{ M/min} = -2.471 \times 10^{-5} \text{ M/s}
\]

\[
\text{Rate}_{\text{series 3}} = \frac{(0.220 - 0.250)}{(29 - 0)} = -0.00103448 \text{ M/min} = -1.724 \times 10^{-5} \text{ M/s}
\]

Thus the reaction rate for each series of experiments was 3.736 x 10^{-5} M/s, 2.471 x 10^{-5} M/s, and 1.724 x 10^{-5} M/s.

**CONCLUSION**

Based on kinetic studies conducted, it could be concluded that nitration of methyl ricinoleate follows a pseudo first-order reaction, the reaction rate for each initial methyl ricinoleate concentration of 0.375, 0.325 and 0.250 M was 3.736 x 10^{-5}, 2.471 x 10^{-5} and 1.724 x 10^{-5} M/s, respectively, at a temperature of 69.6°C. Identification with FTIR, it could be estimated that the results of nitration was a compound containing -NO_3 and -NO_2 groups.

**ACKNOWLEDGEMENT**

Acknowledgements to Staff of Physical Chemistry who prepared the instruments and chemicals for this research.

**REFERENCES**