

KINETICS STUDY ON NITRATION OF METHYL RICINOLEATE

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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 HNO_3 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 3.736×10^{-5} , 2.471×10^{-5} , and 1.724×10^{-5} M/s respectively, with the rate constant at 29 °C was 6.667×10^{-4} (s^{-1}). Based on evaluation of FTIR spectra could be estimated that the nitration produces compounds containing functional groups of $-\text{NO}_3$ and $-\text{NO}_2$.

Keywords: nitration; methyl ricinoleate; kinetics

ABSTRAK

Telah ditentukan nilai parameter kinetika dari reaksi nitration metil risinolat (konstanta laju, orde dan laju reaksi). Reaksi nitration dilakukan dengan HNO_3 maupun asam asetat anhidrit dalam konsentrasi berlebih terhadap metil risinolat. Dengan demikian, nilai parameter kinetika dari reaksi nitration ini hanya dipengaruhi oleh konsentrasi metil risinolat. Berdasarkan pada hasil pengamatan maka dapat disimpulkan bahwa reaksi nitration metil risinolat merupakan reaksi orde 1 semu, konstanta laju reaksi untuk konsentrasi awal sebesar 0,375; 0,325; dan 0,250 M masing-masing adalah sebesar $3,736 \times 10^{-5}$; $2,471 \times 10^{-5}$ dan $1,724 \times 10^{-5}$ M/detik. Berdasarkan hasil pengamatan spektra FTIR dapat diperkirakan bahwa senyawa hasil nitration metil risinolat mengandung gugus fungsi $-\text{NO}_3$ dan $-\text{NO}_2$.

Kata Kunci: nitration; metil risinolat; kinetika

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 HNO_3 and H_2SO_4 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.

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EXPERIMENTAL SECTION

Materials

Some materials used in this study were methyl ricinoleate 98.7% (GC), HNO₃ 65% (Merck), anhydride acetic (Merck), diethyl ether (Merck), anhydrous Na₂SO₄ (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 Hewlett Pacard 5890 seri II).

Procedure

Mol ratio of HNO₃ to methyl ricinoleate (MR) determination

The experiment was intended to determine the optimum mole ratio of HNO₃ 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 HNO₃ and MR were used in this experiment.

Methyl ricinoleate nitration

In the nitration process, initially HNO₃ 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 Na₂SO₄, 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 HNO₃ to methylricinoleate (MR)

No.	Reactant		Mole ratio (HNO ₃ :MR)
	HNO ₃ (mole; mL)	MR (mole; mL)	
1.	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 HNO₃

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 H₂O 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 HNO₃ 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 HNO₃ to MR

HNO₃ is a polar compound, and methyl ricinoleate (MR) has a relatively low polarity. Therefore HNO₃ 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 HNO₃ 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 homogeny. As for the ratio of 25:1 was caused by low concentrations of methyl ricinoleate in the mixture.

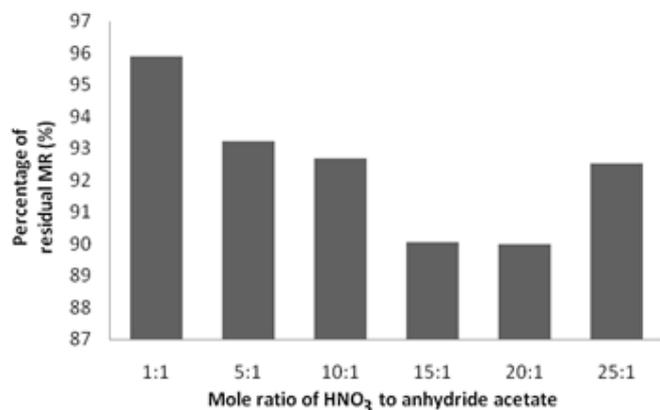


Fig 1. Plot of percentage of residual concentration of MR versus mole ratio of HNO₃ to MR

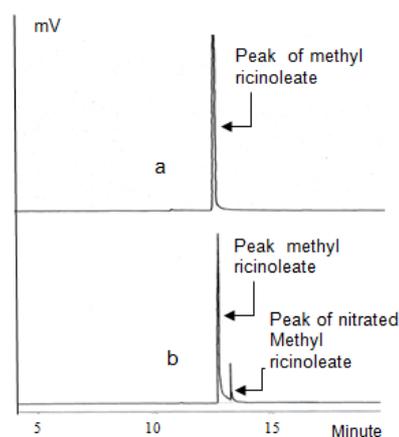


Fig 2. Chromatogram of methyl ricinoleate before nitration (a) and after nitration (b)

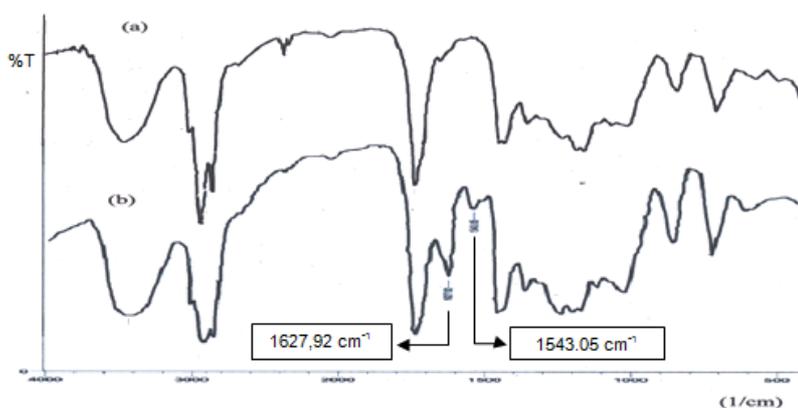


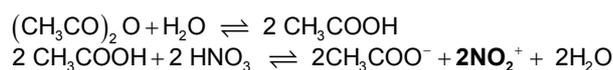
Fig 3. FTIR spectra of methyl ricinoleate before nitration (a) and after nitration for 29 min (b)

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

No.	Wavenumber (1/cm)	Bond (kind of vibration)	Functional group
1.	3421.78	O-H (stretching)	Alcohol
	1246.04	C-O (stretching)	
2.	3009.00	C-H (stretching)	Alkene
	856.41	C-H (bending)	
3.	2927.99	C-H (stretching, antisymmetric)	Alkyl
	2854.70	C-H (stretching, symmetric)	Alkyl
	1462.07; 1438.92 and	C-CH ₂ (stretching)	Methylene
	1361.77	-CH ₃ (stretching)	Methyl
4.	725.25	C-H (stretching)	Long chain alkyl
	1739.82	C=O (stretching)	Ester
5.	1199.74 and 1172.74	C-O (stretching)	Ether

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.



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 4. Concentration of MR after reacted for t min

% (GC)	MR	Ln MR	t (min)
Seri 1 ([MR] ₀ = 0.375 M)			
97.4191	0.365	-1.0079	5
93.2910	0.350	-1.0498	11
92.3294	0.346	-1.0613	17
90.3996	0.339	-1.0818	23
86.3331	0.324	-1.1270	29
Seri 2 ([MR] ₀ = 0.312 M)			
98.5290	0.308	-1.1780	5
96.8851	0.303	-1.1948	11
91.3256	0.285	-1.2539	17
90.1611	0.282	-1.2667	23
88.2172	0.276	-1.2885	29
Seri 3 ([MR] ₀ = 0.250 M)			
96.9155	0.242	-1.4176	5
96.2889	0.241	-1.4241	11
92.5406	0.231	-1.4638	17
90.3648	0.226	-1.4876	23
88.6936	0.222	-1.5063	29

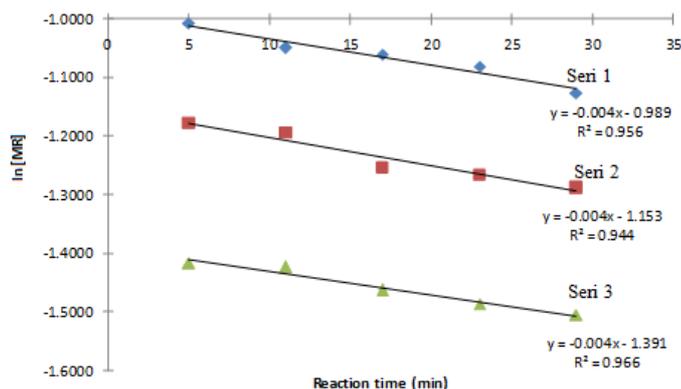
**Fig 4.** Plot of ln MR versus reaction time

Fig. 2a showed that peak of methyl ricinoleate appeared at a retention time of about 12.6 min, while the peak of nitrated methyl ricinoleate appeared at 13.0 min. The concentration of nitrated methyl ricinoleate was 11.42 (% GC) for nitration 29 min (Fig. 2b). Analysis of the products of nitration also be performed with FTIR and compared to the original compound (methyl ricinoleate).

Interpretation of the spectra of methyl ricinoleate (Fig. 3a) in determining the type of bonding and functional groups was listed in Table 3.

Fig. 3b showed two new spectrums that appeared at the wavenumber of 1627.92 and 1543.05 cm^{-1} . The existence of $-\text{NO}_3$ group was marked by a sharp absorption spectrum in the region 1650-1500 cm^{-1} [14], while the $-\text{NO}_2$ group was marked by a sharp spectrum at region of 1550-1372 cm^{-1} and a spectrum with moderate intensity in the region of 1390-1300 cm^{-1} . According to Suppes at al. [5], the formation of nitrate compound ($-\text{NO}_3$ group) was marked by spectrum at 1650, 1282 and 854 (cm^{-1}), meanwhile for nitro

compounds ($-\text{NO}_2$ group) were characterized by the wavenumber spectrum at 1553 and 1375 cm^{-1} . Based on this information could be estimated that compound which was resulted from nitration of methyl ricinoleate was a molecules 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 ([MR]₀) could be expressed as:

$$r = \frac{dx}{dt} = k [\text{HNO}_3]^v [\text{AA}]^w ([\text{MR}]_0 - x)^q \quad (1)$$

Because the concentration of HNO_3 and AA can be considered constant, then equation 1 turns into equation 2 and 3.

$$r = k' ([\text{MR}]_0 - x)^q \text{ wherein } k' = k [\text{HNO}_3]^v [\text{AA}]^w \quad (2)$$

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:

$$\ln [\text{MR}] = \ln [\text{MR}]_0 - kt \quad (3)$$

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

Table 4 showed the concentration of residual methyl ricinoleate ([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 [MR]₀, so that [MR] after the reaction could be determined. Furthermore, the data [MR] was converted into $\ln [\text{MR}]$, 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 4×10^{-3} , so that the rate constant value (k) was equal to $4 \times 10^{-3} (\text{min}^{-1})$ or equal to $6.667 \times 10^{-4} (\text{s}^{-1})$.

On series different initial concentrations, the change concentration of MR with time of reaction were monitored. So by plotting [MR] versus time a reaction rate was evaluated from slope. The slope was obtained by drawing a tangent curve starting from $t = 0$.

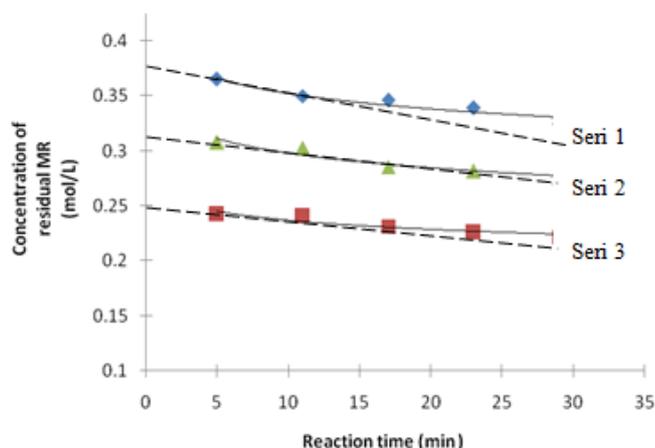


Fig 5. Plot of residual concentration of MR versus time of reaction

Based on Fig. 5, and then carried out the calculation as follows:

$$\text{Rate}_{\text{seri 1}} = \frac{(0.310 - 0.375)}{(29 - 0)}$$

$$= -0.00224138 \text{ M/min} = -3.736 \times 10^{-5} \text{ M/s}$$

$$\text{Rate}_{\text{seri 2}} = \frac{(0.270 - 0.312)}{(29 - 0)}$$

$$= -0.00148276 \text{ M/min} = -2.471 \times 10^{-5} \text{ M/s}$$

$$\text{Rate}_{\text{seri 3}} = \frac{(0.220 - 0.250)}{(29 - 0)}$$

$$= -0.00103448 \text{ M/min} = -1.724 \times 10^{-5} \text{ M/s}$$

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

CONCLUSION

Based on kinetic studies conducted, it could be concluded that nitration of methyl ricinoleate follows pseudo first-order reaction, the reaction rate for each initial methyl ricinoleate concentration of 0.375, 0.325 and 0.250 M was 3.736×10^{-5} , 2.471×10^{-5} and $1.724 \times 10^{-5} \text{ M/s}$, meanwhile reaction rate constant at 29 °C of $6.667 \times 10^{-4} \text{ (s}^{-1}\text{)}$. Identification with FTIR, it could be estimated that the results of nitration was a compound containing $-\text{NO}_3$ and $-\text{NO}_2$ groups.

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