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ACTIVE INTERMEDIATE REACTION MECHANISM FOR NITROCELLULOSE PRODUCTION

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Abstrak

Salah satu produk turunan selulosa yang paling banyak diaplikasikan di dalam industri adalah nitroselulosa yang dihasilkan melalui reaksi nitrasi antara selulosa dan asam nitrat. Pada penelitian ini diteliti penentuan mekanisme reaksi *active intermediate* produksi nitroselulosa. Empat model mekanisme *active intermediate* dipakai untuk memprediksi reaksi pembentukan nitroselulosa. Berdasarkan hasil penelitian diperoleh bahwa model 3 dan 4 merupakan model *active intermediate* yang tidak mempertimbangkan pengaruh katalis asam sulfat dalam reaksi nitrasi dengan sifat reaksi nitrasi yang irreversible. Ion NO_2^+ merupakan senyawa *active intermediate* yang memiliki peranan penting dalam memproduksi nitroselulosa. Asam sulfat pada reaksi nitrasi berfungsi untuk memecah asam nitrat menjadi ion NO_2^+ tanpa mempengaruhi proses nitrasi selulosa.

Kata kunci: active intermediate, nitroselulosa, nitrasi, selulosa.

Abstract

One of the most widely applied cellulose derivative products in industry is nitrocellulose which was produced through a nitration reaction between cellulose and nitric acid. In this research, the determination of the active intermediate reaction mechanism for nitrocellulose production was investigated. Four active intermediate mechanism models were used to predict the nitrocellulose formation reaction. Based on the results, it was found that models 3 and 4 which were active intermediate models that did not consider the effect of the sulfuric acid catalyst in the nitration reaction with irreversible nitration reaction. NO_2^+ ion was an active intermediate compound which had an important role in producing nitrocellulose. Sulfuric acid in the nitration reaction used to break down nitric acid into NO_2^+ ions without affecting the cellulose nitration process.

Keywords: *active intermediate, nitrocellulose, nitration, cellulose.*

1. INTRODUCTION

Nitrocellulose is a cellulose derivative product that produced from cellulose and nitric acid through a nitration reaction (Seta et al., 2014). The used of nitrocellulose in industry has many applications such as plastics, paint, adhesive and rocket fuel (propellant) industries. In the explosives material, nitrocellulose will be converted into propellant which applied to a Folded Fin Aerial Rocket (FFAR) type rocket. FFAR is a double base type propellant which the main composition were nitrocellulose and nitroglycerin and used by the Indonesian armed forces (Miranda, 2015). Global nitrocellulose needs were predicted to be increase every year. According to Grand View Research (2018), nitrocellulose needs will increase around 6.1% until 2024 to fulfill nitrocellulose needs for industrial applications such as printer inks, paints, wood coatings, leather finishes and nail varnishes (Grand View Research, 2018).

Several studies have investigated the cellulose nitration reaction. Sun et al (2022) investigated the thermal stability of nitrocellulose against nitric acid and sulfuric acid. Baumann et al (1982) investigated the production of nitrocellulose without sulfuric acid. Stovbun et al (2016) investigated the physical mechanism of cellulose nitration reaction kinetics. Ikhsanov et al (2020) investigated nitrocellulose production under supercritical conditions. Short and Munro (1993) investigated nitrocellulose production by X-ray photoelectron spectroscopy and nuclear magnetic resonance analysis. Cheung (2014) investigated cellulose nitration for membrane applications. Ronggur (2012) investigated reaction kinetics of palm oil frond waste nitration process.

Based on various studies of cellulose nitration reactions that have been carried out, there has been no research examining the mechanism of nitrocellulose production reaction. Nitrocellulose reaction associated with the binding of ionic groups into cellulose material includes active intermediate reactions. Therefore, in this study, the reaction mechanism of active intermediate in the nitrocellulose production with cellulose, nitric acid and sulfuric acid as catalysts was investigated.

2. METHOD

The basic reaction for nitrocellulose production can be seen in Figure 1. Nitrocellulose was formed by nitration reaction between cellulose and nitric acid using sulfuric acid catalyst. The basic reaction for nitrocellulose production was then broken down into the active intermediate mechanism according to Table 1.

$$\mathrm{Cell} + 2HNO_3 \xrightarrow[k]{H_2SO_4} \mathrm{NCell} \quad \ldots (1)$$

Figure 1. Nitrocellulose Formation Reaction

Based on Table 1, the active intermediate mechanism of cellulose nitration reaction will be divided into four models. Model 1 was a model that considered the effect of sulfuric acid catalyst in a nitration reaction with a reversible nitration reaction. Model 2 was a model that considered the effect of sulfuric acid catalyst in a nitration reaction with an irreversible nitration reaction. Model 3 was a model that did not consider the influence of sulfuric acid catalyst in an irreversible nitration reaction. While model 4 was a model that used the breakdown of nitric acid into NO_2^+, NO_3^- and water ions. The four models will be derived to find out which model was the most suitable for obtaining the main active intermediate reaction for nitrocellulose production according to the equation:

$$r_{Ncell} = k_5.\mathrm{Cell}.[NO_2^+] \ \ldots (2)$$

Table 1. Nitrocellulose Reaction Mechanism Model

Model Type	Reaction Mechanism
Model 1	$H_2SO_4 \xrightarrow{k_1} SO_4^{2-} + 2H^+$ … (3) $SO_4^{2-} + 2H^+ \xrightarrow{k_2} H_2SO_4$ … (4) $HNO_3 + H^+ \xrightarrow{k_3} NO_2^+ + H_2O$ … (5) $NO_2^+ + H_2O \xrightarrow{k_4} HNO_3 + H^+$ … (6) $\mathrm{Cell} + NO_2^+ \xrightarrow{k_5} \mathrm{NCell}$ … (7) $\mathrm{NCell} \xrightarrow{k_6} \mathrm{Cell} + NO_2^+$ … (8)
Model 2	$H_2SO_4 \xrightarrow{k_1} SO_4^{2-} + 2H^+$ $SO_4^{2-} + 2H^+ \xrightarrow{k_2} H_2SO_4$ $HNO_3 + H^+ \xrightarrow{k_3} NO_2^+ + H_2O$ $NO_2^+ + H_2O \xrightarrow{k_4} HNO_3 + H^+$ $\mathrm{Cell} + NO_2^+ \xrightarrow{k_5} \mathrm{NCell}$
Model 3	$HNO_3 + H^+ \xrightarrow{k_3} NO_2^+ + H_2O$ $NO_2^+ + H_2O \xrightarrow{k_4} HNO_3 + H^+$ $\mathrm{Cell} + NO_2^+ \xrightarrow{k_5} \mathrm{NCell}$
Model 4	$2HNO_3 \xrightarrow{k_3} NO_2^+ + NO_3^- + H_2O$ … (9) $NO_2^+ + NO_3^- + H_2O \xrightarrow{k_4} 2HNO_3$ … (10) $\mathrm{Cell} + NO_2^+ \xrightarrow{k_5} \mathrm{NCell}$

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3. RESULTS AND DISCUSSION

Model 1 Evaluation

Based on Table 1 and equation (2), it was necessary to find the value of $[NO_2^+]$ according to model 1:

$r[NO_2^+] = k_3.[HNO_3].[H^+] - k_4.[NO_2^+].[H_2O] - k_5.Cell.[NO_2^+] + k_6.NCell$ … (11)

it was assumed that $r[NO_2^+] = 0$ because NO_2^+ ion will be directly used to form nitrocellulose, then equation (11) become:

$$[NO_2^+] = \frac{k_3.[HNO_3].[H^+]+k_6.NCell}{k_4.[H_2O]+ k_5.Cell} \ldots (12)$$

Based on equation (12), it was necessary to know the value of H^+ ion based equation:

$r[H^+] = k_1.[H_2SO_4] - k_2.[SO_4^{2-}].[2H^+] - k_3.[HNO_3].[H^+] + k_4.[NO_2^+]+.[H_2O]$ … (13)

assumed $r[H^+] = 0$, then:

$$[H^+] = \frac{k_1.[H_2SO_4]+k_4.[NO_2^+].[H_2O]}{k_4.[SO_4^{2-}].[H^+]+ k_3.[HNO_3]} \ldots (14)$$

Equation (14) was a complex equation because the value of SO_4^{2-} and H^+ ions which originating from the decomposition of sulfuric acid according to equation (3) needed to be knew. Therefore, it was necessary to change the model, which assumed that the effect of sulfuric acid was insignificant, so that it can be ignored according to models 3 and 4. If H^+ ion did not involve in equation (3), then the H^+ ion becomes:

$$[H^+] = \frac{k_4.[NO_2^+].[H_2O]}{k_3.[HNO_3]} \ldots (15)$$

Equation (15) was then inserted into equation (12) to become:

$$[NO_2^+] = \frac{k_6.NCell}{k_5.Cell} \ldots (16)$$

Equation (16) was then inserted into equation (2) to become rNcell = 0. Based on the derivation of the model that has been done, it can be seen that model 1 cannot be used for nitrocellulose production reaction mechanism.

Model 2 Evaluation

Model 2 was a modification of model 1 considering that the nitrocellulose production reaction was irreversible while still considering the effect of sulfuric acid. The nitrocellulose production reaction can be irreversible because the decomposition process of nitrocellulose requires heat [4]. From model 2, the equation for finding the value of $[NO_2^+]$ was obtained:

$r[NO_2^+] = k_3.[HNO_3].[H^+] - k_4.[NO_2^+].[H_2O] - k_5.Cell.[NO_2^+]$ … (17)

it was assumed that $r[NO_2^+] = 0$ because the ions will be directly used to form nitrocellulose, then equation (17) becomes:

$$[NO_2^+] = \frac{k_3.[HNO_3].[H^+]}{k_4.[H_2O]+ k_5.Cell} \ldots (18)$$

To find the H^+ ion value, it was necessary to assumed that there was no effect of sulfuric acid in the reaction, so that the H^+ equation was obtained according to equation (15). Equation (15) was then included in equation (17) to obtain $[NO_2^+] = 0$. Therefore, it can be seen that model 2 cannot be used for nitrocellulose reaction mechanism production.

Model 3 Evaluation

Model 3 was a modification of model 2 by removing the effect of sulfuric acid on the nitrocellulose formation reaction. Sulfuric acid is a catalyst for breaking down nitric acid to produce NO_2^+ ions. In various studies, NO_2^+ ion determined the process to forming nitrocellulose. Therefore, removing the sulfuric acid breakdown step in the nitrocellulose production reaction can be carried out to determine the mechanism of nitrocellulose production. The large number of NO_2^+ ions needed in the reaction so that nitrocellulose can be formed. Model 3 stated that $r[NO_2^+] \neq 0$. In model 3, it was necessary to find the value of $[NO_2^+]$ according to equation (17). To find the value of the ion [H+], equation (15) was used so that after being entered into equation (17) we got:

$r[NO_2^+] = -k_5.Cell.[NO_2^+]$ … (19)

Equation (19) was other version of equation (2) based on equation (7) so that model 3 can be used for the reaction mechanism for nitrocellulose production.

Model 4 Evaluation

Model 4 was a mechanism for nitrocellulose production where nitric acid was broken down into three products namely NO_2^+, NO_3^- and water ions according to research Short and Munro (1993). Model 4 was an affirmation to state the role of NO_2^+ ions in nitrocellulose production. In this model, it was stated that $r[NO_2^+] \neq 0$ so that the equation $r[NO_2^+]$ in model 4 was obtained:

$r[NO_2^+] = k_3.[2HNO_3] - k_4.[NO_2^+].[NO_3^-].[\ H_2O] - k_5.Cell.[NO_2^+]$ … (20)

To find the value of NO_3^-, used $r[NO_3^-] = 0$ because NO_3^- ion did not take part in the reaction so

$r[NO_3^-] = k_3.[2HNO_3] - k_4.[NO_2^+].[NO_3^-].[\ H_2O] = 0$ … (21)

then the equation becomes:

$$[NO_3^-] = \frac{k_3.2HNO_3}{k_4.[NO_2^+].H_2O} \ldots (22)$$

Equation (22) was then incorporated into equation (20) to become equation (19) so that model 4 can be used for the reaction mechanism for nitrocellulose production.

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4. CONCLUSION

In this research, the determination of nitrocellulose reaction mechanism with active intermediates was investigated. Based on the reaction mechanism model tested, it was found that models 3 and 4 are models that can present the reaction mechanism for nitrocellulose formation. Models 3 and 4 focus on nitrocellulose irreversible formation from NO_2^+ ions. Based on these two models, NO_2^+ ion is an active intermediate compound that had an important role in producing nitrocellulose. Sulfuric acid as catalyst in nitrocellulose production process functioned to break down nitric acid to produce NO_2^+ ions without affecting the cellulose nitration process.

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