Indonesian Journal of Chemistry and Environment
Vol. 8, No. 2, December 2025, pp. 71~77
e-ISSN: 2599-3186

TLC Monitoring on The Auto Reduction-Oxidation Reaction of Benzaldehyde Derivatives in Alcohol-Water as Solvent System

Dini Rohmawati*, Sri Handayani*, Cornelia Budimarwanti*, Dina Wahyu Handayani[1], Febrian Ayu Puspitasari[1], Kirei Irawanti Muthmainnah[1]
* Department of Chemistry Education, Universitas Negeri Yogyakarta

Article Info

Article history:

Received Dec 16th, 2025
Revised Dec 26th, 2025
Accepted Aug 31st, 2025

Corresponding Author:

Dini Rohmawati,
Dep. of Chemistry Education
Universitas Negeri Yogyakarta

Email: dini_rohmawati@uny.ac.id

ABSTRACT

Autoreduction-oxidation reactions of benzaldehyde derivatives could be done without solvent, solventless, and with solvent conditions. Green solvents are one method to reduce the use of nonenvironmentally friendly solvents by considering their effectiveness in yielding. Benzaldehyde derivatives and NaOH were reacted in comparison of 1 : 1 with various alcohol-aquadest (0%, 20%, 50%, 80%, and 100%) as solvent system. The procedure for this disproportionation reaction is focused on grinding and ultrasonic-assisted methods. Both procedures could be applied under all solvent conditions along with the effective and efficient processes hence it corresponds to the green chemistry principles and sustainable development goals (SDGs). This article discussed the monitoring of product reaction using thin layer chromatography (TLC) techniques to evaluate the procedures of grinding and ultrasonic-assisted on the disproportionation reactions, which later could be used as standard procedures according to green chemistry and sustainable development goals (SDGs).

Keyword: benzaldehyde derivatives, autoreduction-oxidation, solvent, grinding

1. INTRODUCTION

As environmental awareness becomes a more substantial issue, various methods and procedures in chemical preparation are introduced to support this topic. Solvents in chemical reactions are essential parts as they could be used to form solvation with the reagent and enhance the molecules in the formation of the product which lead to the increase in kinetic rate reaction (Slakman & West, 2018). However, several solvents are considered quite harmful to the environment. Therefore, implementing methods or procedures by considering the type of solvent becomes more beneficial for researchers. Among the commonly used solvents for chemical reactions that are considerably environmentally friendly are alcohol and water (Mainkar et al., 2024). Disproportionation reactions could also be conducted under nonsolvent, solventless, and solvent conditions. This reaction is an auto reduction–oxidation reaction on the benzaldehyde derivatives without hydrogen in the alpha position. Several procedures use nonenvironmental-friendly solvents to promote the collision of the molecules between reactants. However, because of the discord with the green chemistry principles, an environmentally friendly solvent is used as a substitute in the reaction.

The disproportionation reaction of aldehyde without alpha hydrogen refers to the Cannizzaro reaction. Theoretically, this reaction known due to the result gave percent yields about

50% of alcohol and 50% of carboxylic acid in one single-step reaction. The formation of the two products occurred due to the presence of a strong base such as NaOH which leads the carbon atom of carbonyl to undergo nucleophilic acyl substitution. The abstract of hydroxy ions leads to the formation of alkoxide ions as an ionic mechanism (Suhail et al., 2020). In addition, the presence of solvents could also promote the reaction by increasing the solvation and kinetic rate. Since the common starting materials are semipolar - polar compounds, polar solvents are generally used to enhance the effectiveness of the reaction. Further, an ionic solution also introduced as eco-friendly solvent system in Cannizzaro reaction (Daemi et al., 2016). In the preparation for the undergraduate practicum, the effectiveness of procedure in reaction usually is observed under thin layer chromatography (TLC). This technique offered a simple and convenient separation method based on the polarity of organic compound in the mixture (Silver, 2020). TLC also offers fast results to confirm the reaction product such as the formation of the target molecule, the decrease of the starting materials, and the appearance of byproduct (Hemmateenejad et al., 2012). The analysis from TLC gave information of polarity of the product from the Rf value and the eluent system (Dickson et al, 2004). Herein, the Cannizzaro reaction which was conducted in environmentally friendly procedures: grinding and ultrasonic-assisted methods with solvent to assist the reaction was monitored by TLC to confirm the effectiveness of the method for several benzadehyde derivatives.

2. RESEARCH METHOD

All of chemicals were used as it was obtained without further purification. Benzaldehyde derivatives: benzaldehyde, *p*-anisaldehyde, and vanillin. The solvent in this experiment is alcohol (methanol or ethanol) in water with concentrations of 0, 20, 50, 80, and 100%. TLC was monitored under UV lamp 254 nm.

General procedure for grinding method: Benzaldehyde derivatives (0.1 mmol), NaOH (0.1 mmol), and 0.5 mL solvents were ground in mortar-pestle for 10 minutes. Upon completion, the mixture was poured into cold aquades, acidified with 2 M HCl, and followed by filtration to get the precipitation as acid product. The filtrat was extracted with ethyl acetate (3 x 10 mL), dried over Na_2SO_4, and evaporated it to give alcohol product. Product acid and alcohol were then monitored using TLC with eluent system n-hexane : ethyl acetate (2 : 1, v/v) in room temperature in the 5 x 5 cm of chamber.

General procedure for ultrasonic-assisted method: Benzaldehyde derivatives (0.1 mmol), NaOH (0.1 mmol), and aquades (5 mL) were put in the vial and place it on the sonicator. The reaction was done within 10 minutes. Upon completion, 5 mL aquades were added and water layer was acidified to precipitate the acid product. The organic layer was extracted with ethyl acetate (3 x 10 mL), dried over with Na_2SO_4, and evaporated it to give alcohol product. Product acid and alcohol were then monitored using TLC with eluent system n-hexane : ethyl acetate (2 : 1, v/v) in room temperature in the 5 x 5 cm of chamber.

3. RESULTS AND ANALYSIS

With aiming to prepare a simple procedure for undergraduate practicum, the experiment in Cannizzaro reaction was conducted by using convenient materials. Two methods, grinding and sonication, were used to assist the molecule collosion. In addition, the methods also applied the enviromentally-friendly procedure in organic chemistry praticum. The Cannizzaro reaction between benzadehyde derivatives and sodium hydroxide gave reduction and oxidation products.

Initial procedure was derived from previous work by varying the concentration of base and the good results showed from the comparison of 1 : 1 between benzaldehyde derivatives and base. Accordingly, this work adopted the concentration of reagents with the method of grinding and ultrasonic-assisted as showed in **Figure 1**. The condition for the reactions were set in room temperatur within 10 minutes (the monitoring results by TLC) using methanol or ethanol in various concentration (0 – 100%). The use of solvents in reactions takes into account their suitability for dissolving reagents and also facilitating the process.

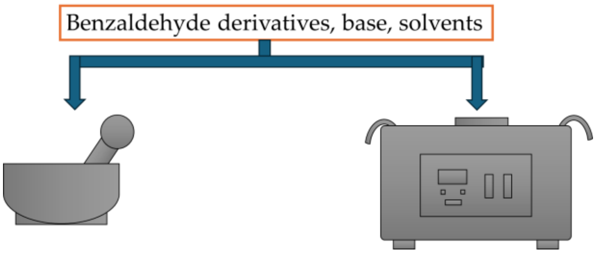


Figure 1. The simplified diagram of experiment method.

TLC was then prepared separately to ensure the saturated condition in the chamber. Filter paper could be use to assist in saturating the chamber as shown in **Figure 2**. The developed eluent system was n-hexana : ethyl acetate (2 : 1, v/v).

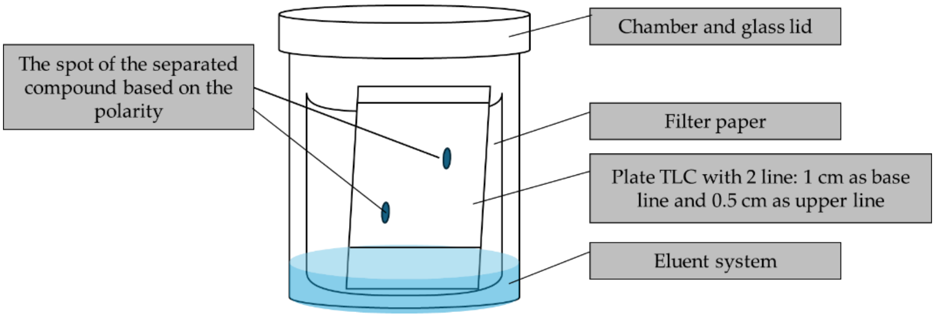


Figure 2. Setting up the chamber for TLC of organic compound (adapted from Silver, 2020).

Accordingly, the TLC plate picked up after the eluent reached the solvent front see **Figure 3**. In case of new spot appeared in the within those distance, then the value of retention factor, Rf, could be determined. In auto reduction – oxidation of benzaldehyde derivatives, there are three possibility of spots: from aldehyde (as starting material), from alcohol (as reduction product), and from carboxylic acid (as oxidation product). If the aldehyde spot still appear, it could be

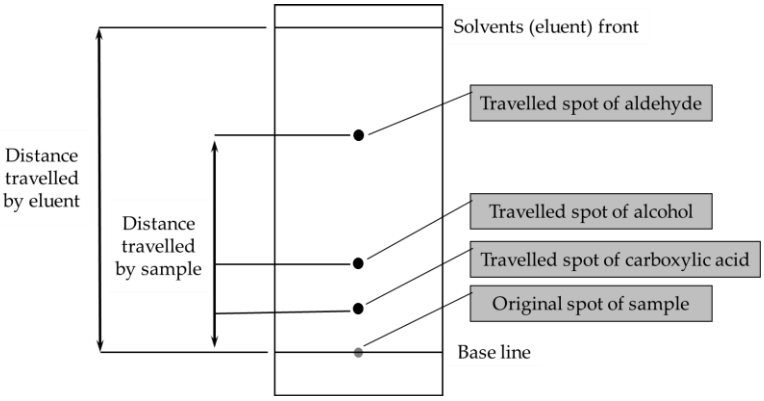


Figure 3. Determination Rf in TLC from autoreduction-oxidation reaction of benzadehyde derivatives (adapted from Dickson et al., 2004).

During the experiment, the monitored reaction products using TLC were depicted in **Table 1**, **2**, and **3** as product I for acid and product II for alcohol. Solvent system for the reaction (methanol, MeOH in water and ethanol, EtOH): 0, 20, 50, 80, and 100% (from left to right).

Table 1. TLC monitoring of reaction products from benzaldehyde and NaOH under UV 254 nm

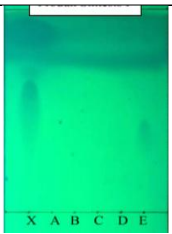
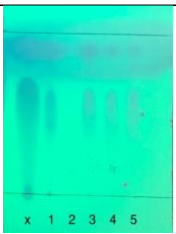
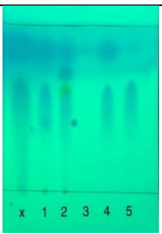
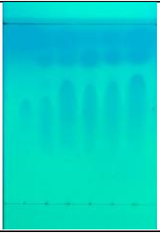
Methods	Methanol		Ethanol	
	Product acid	Product alcohol	Product acid	Product alcohol
Grinding				
Ultrasonic-assisted				

Table 2. TLC monitoring of reaction products from *p*-anisaldehyde and NaOH under UV 254 nm.

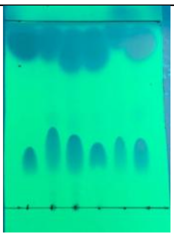
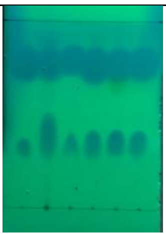
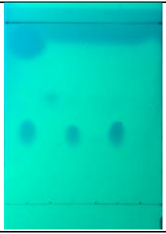
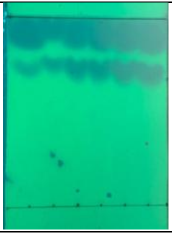
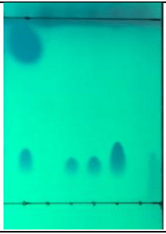
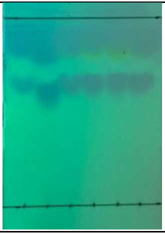
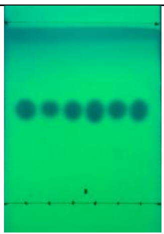
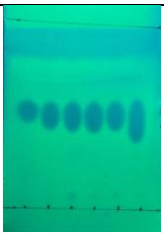
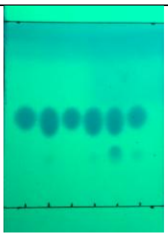
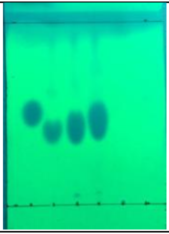
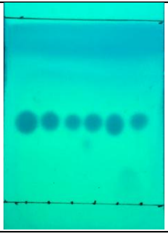
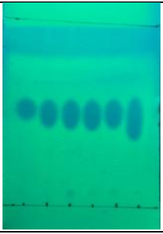
Methods	Methanol		Ethanol	
	Product acid	Product alcohol	Product acid	Product alcohol
Grinding				
Ultrasonic-assisted				

Table 3. TLC monitoring of reaction products from vanillin and NaOH under UV 254 nm.

Methods	Methanol		Ethanol	
	Product acid	Product alcohol	Product acid	Product alcohol
Grinding				
Ultrasonic-assisted				

TLC monitoring after the 10-minute reaction showed different results from the three starting materials. For benzaldehyde and p-anisaldehyde, products formed in both methods even though the reaction was incomplete. Meanwhile, for vanillin, the changes were insignificant. Therefore, the method and reaction time need to be reconsidered. This difference may be due to the structure of vanillin, which has a hydroxyl group attached to the benzene ring in para position, resulting in additional active reaction sites aside from the aldehyde group as shown in **Figure 4**. The strong basic in the system could lead to deprotonation of the proton on the hydroxy group and give the vanillin phenoxide ion (Alunga et al., 2015). The electron-rich of oxygen atom on phenoxide ion lead to the the stabilization of carbonyl side through electron delocalization which later decrease the electrophile character of carbon – carbonyl and made it unresponsive to give Cannizzaro products (Barbera et al., 2018). Therefore, the Cannizzaro reaction of vanillin should be under different condition compare to benzaldehyde and p-anisaldehyde.

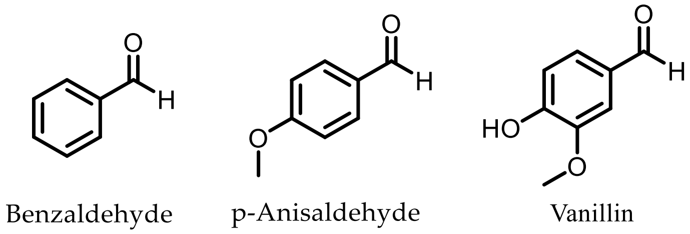


Figure 4. Structure of starting materials.

In addition, since Cannizzaro reaction gave two products, the results displayed the uncomplete separation of the compounds. The difference of polarity from the starting material and two products is increase gradually. An aldehyde as starting material is the less polar character, alcohol with polar character, and and carboxylic acid with the most polar character. Therefore, the separation should be from the highest to the lowest: aldehyde, alcohol, and carboxylic acid (see **Figure 3**). In case the separation is not complete, this could be from the unsuitable eluent system. Therefore, it is recommended to try another eluent system to facilitate the separation and give better developing system of TLC. In several spots, it also be observed the tailed spot due to the polarity of the sample which made it bind stronger to the solid phase (see **Figure 5**). In this case, more polar developing system is recommended. However, if the sample is a mixture, the high polarity of eluent may give hig Rf value from non or less polar compound. To ensure the best separation spot, several experiment for the developing system usually in saturated condition is needed (Silver, 2020). While for the disappearance of spot, it could be from the concentration initial spot is too low. Hence, multipling application of the initial spot for low concentration sample is prescripted. Conversely, if the initial spot or resulted spot is big, it could be from the big hole of the needle or the high concentration of the sample which transfer a lot of sample to the plate. The solution is either change to the smaller hole needle or dilute the sample to lower its concentration.

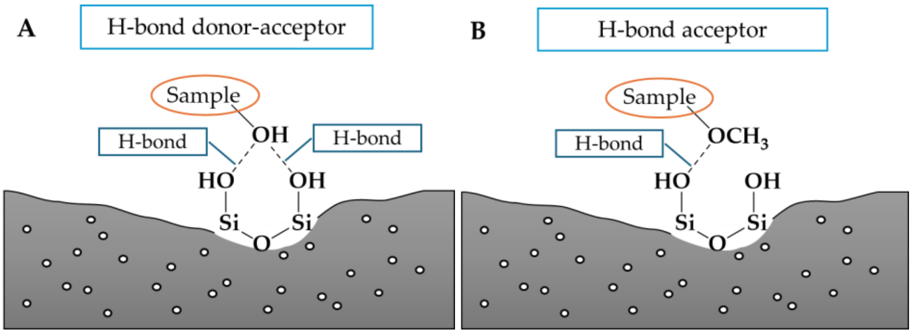


Figure 5. H-bonding interaction in silica gel for polar sample, **A**, and less polar sample, **B** (adapted from Dickson et al., 2004).

The two methods of reaction also showed a similar trends in the results of benzaldehyde and *p*-anisaldehyde. Both methods offer the enhancement in the interaction between starting materials. In grinding, the friction between mortar and pestle during the process increased the probalitity of molecules in collision by decreasing its size. The use of solvents in this method aims to accelerate chemical transformation and increase the probability of chemical conversion due to slow reaction rates (Fiss et al., 2021). However, the amount of the solvent is in very small quantity. Hence, this method offer a shorter reaction time and less solvent compare to the traditional method. In similar purpose, ultrasonic assisted method also developed to assist the reaction by increasing the probability of the molecules in collision. By the oscillation of pressure waves in liquid phase, cavitation phenomena was formed. This occurence due to the trapped gas in the fissure of solid surface (Li & Ashokkumar, 2018). The phenomenon can affect the chemical and physical aspects of the molecule when the bubble collapsed and send the shock wave through the medium. Accordingly, the wave can mitigate the mass and energy transfer which lead to the formation intermolecular collision and modification of the particle surface (Martínez et al., 2021). Nevertheless, both grinding and ultrasound assisted method encouraged the acceleration of the reduction and oxidation in benzaldehyde and p-anisaldehyde within short time (10 minutes).

Interestingly, the solvent system showed a significant difference in benzaldehyde and *p*-anisaldehyde. The reaction in ethanol-water system gave a promising results compare to the methanol-water system in separation. These results indicated that Cannizzaro reaction could be done in the harmless and environment-friendly solvent. While for vanillin, the difference is vague with tailed separation spots for the reduction products. It was suggested that vanillin may react with the bases to form product.

4. CONCLUSION

The TLC monitoring of two products from the Cannizzaro reaction of benzadehyde derivatives (specifically, benzadehyde and p-anisaldehyde) in methanol and ethanol solvent gave separation spots in accordance as acid and alcohol products. Several noted from the results need to be consider for the future experiment are the use of suitable developing system, optimization of reaction time, and an appropriate method for hydroxybenzaldehyde derivatives. In addition, the Cannizzaro reaction in ethanol showed a promising results as suggested from the TLC.

ACKNOWLEDGEMENTS

This research was funded by Faculty Mathematics and Natural Sciences under the Research Group Grant No B/34/UN34.13/PM.01.01/2024.

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