Kinetic Study of the Reaction between 7-Methoxy-1-Tetralone and Glyoxylic Acid via Basic Catalysis

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INTRODUCTION & AIM

1-Tetralones are compounds widely used as raw materials in organic synthesis due to their molecular versatility for the design of molecules with applications in various industrial fields. In particular, 7-Methoxy-1-tetralone stands out for its pharmacological activity and as an intermediate in the synthesis of compounds such as dyes, pesticides, among others[1-3]. Based on this evidence, the present study aimed to investigate the kinetics of the Knoevenagel condensation reaction between 7-Methoxy-1-tetralone (1), glyoxylic acid (2), and potassium *tert*-butoxide as a catalyst. The reaction was carried out at three temperatures (65, 75, and 85 °C), monitoring the progress over time using TLC and HPLC for the production of (*E*)-2-(7-Methoxy-1-oxo-3,4-dihydronaphthalen-2(1*H*)-ylidene)acetic acid (3). The experimental results allowed for the identification of the kinetic parameters of the reaction and the mathematical models that best fit and maximized the yield. Fig. 1 shows the general reaction.

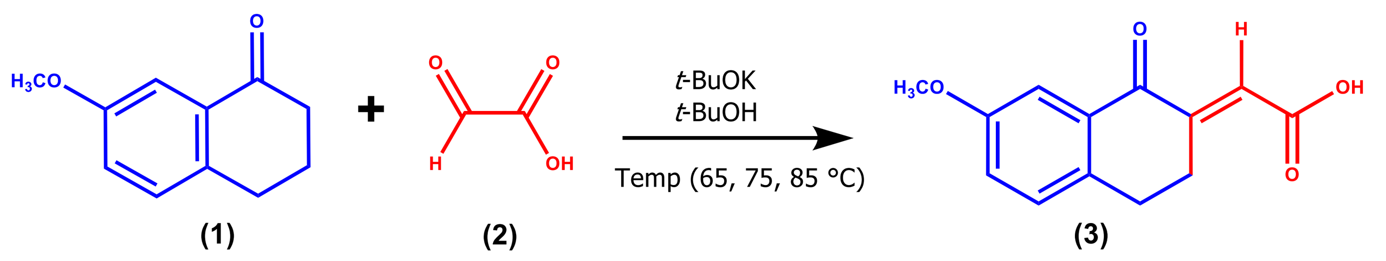
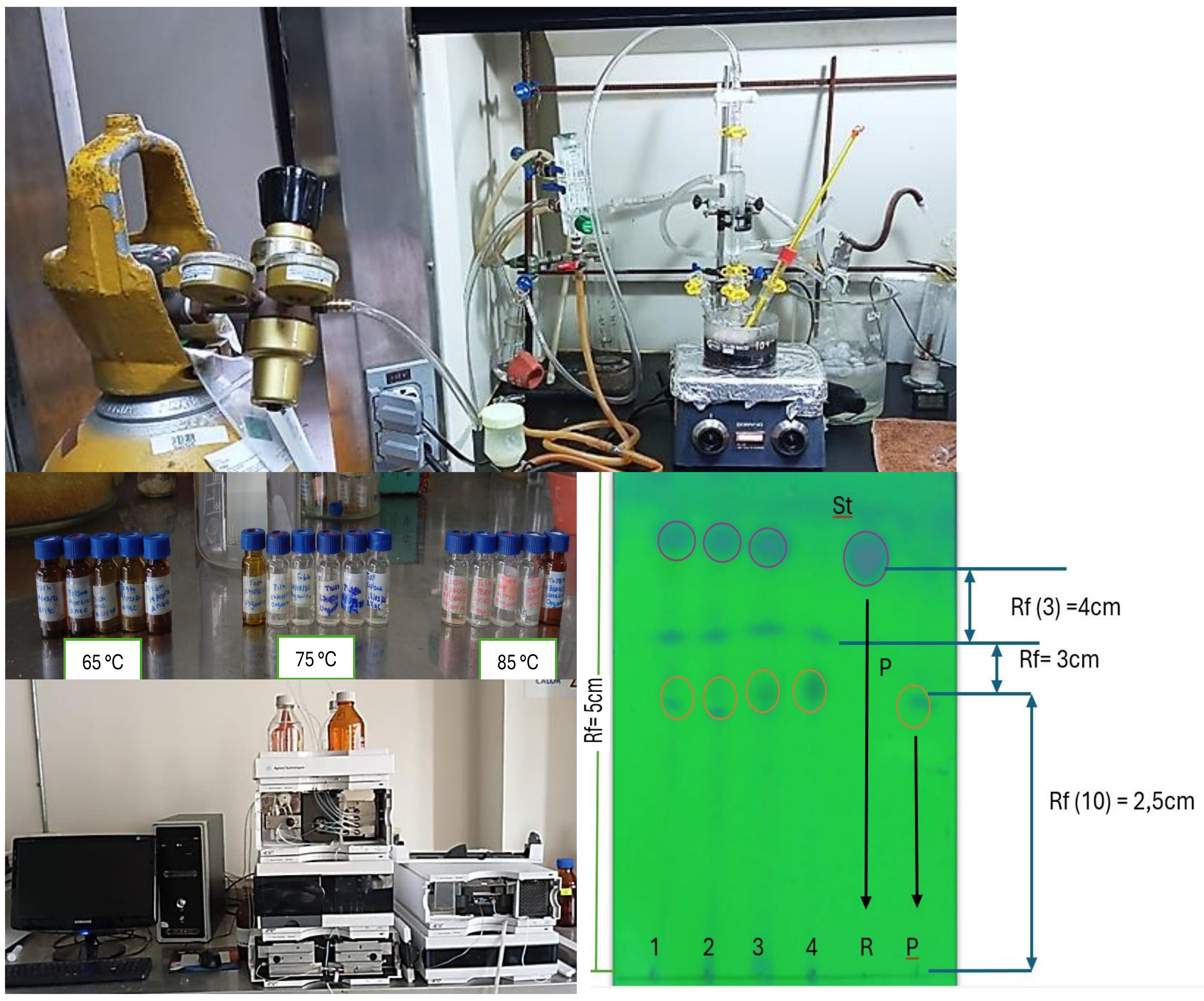


Figure 1. Knoevenagel condensation reaction to obtain (3).

METHOD

The reaction was carried out in a batch system under a nitrogen atmosphere. In a three-neck flask equipped with a thermometer, connectors, and a condenser, the reactants (1), (2) were placed, using *tert*-butanol as the solvent and *tert*-BuOK as catalyst. The mixture was heated in an oil bath at the study temperatures (65, 75 and 85 °C) with constant stirring at 600 rpm. The conversion was monitored using thin-layer chromatography (TLC) and high-performance liquid chromatography (HPLC) at defined time intervals. The product was purified by recrystallization in ethanol and characterized using FTIR, UV-Vis, and GC-MS. The kinetic data were analyzed using mathematical methods: integral, differential, and nonlinear regression.



St: Reactant, P: product

RESULTS & DISCUSSION

The unsaturated acid (3) was obtained under experimental conditions at a temperature of 75 °C over a period of 28 hours, with a total yield of 81.40 %. In contrast, at temperatures of 65 °C and 85 °C, the yields were 17.01 % and 72.59 %, respectively, and total conversion was not achieved. The kinetic study showed that the model that best fitted was the pseudo-second order model, determined through nonlinear regression, with a rate constant of 1.77 mL mmol^{-1} min^{-1}. The calculated activation energy was 67.22 kJ mol^{-1}, and the pre-exponential factor was 2.19×10^{10} mL mmol^{-1} min^{-1}, indicating that the reaction is favorable. Spectroscopic characterization confirmed the identity of the unsaturated acid (3) with good purity.

Table 1. Results of the kinetic parameters

Parameters	1	2	3
Temperature [°C]	65	75	85
Time [h]	28	28	6
Yield [%]	17.01	81.40	72.59
Reaction Order [α]	2.01	2.05	2.00
k$\left[\left(\frac{mL}{mmol*min}\right)^{\propto-1}\right]$	0.89	1.77	3.42
Ea $\left[\frac{kJ}{mol}\right]$		67.22	
A $\left[\left(\frac{mL}{mmol*min}\right)^{\propto-1}\right]$		$2.19x10^{10}$	

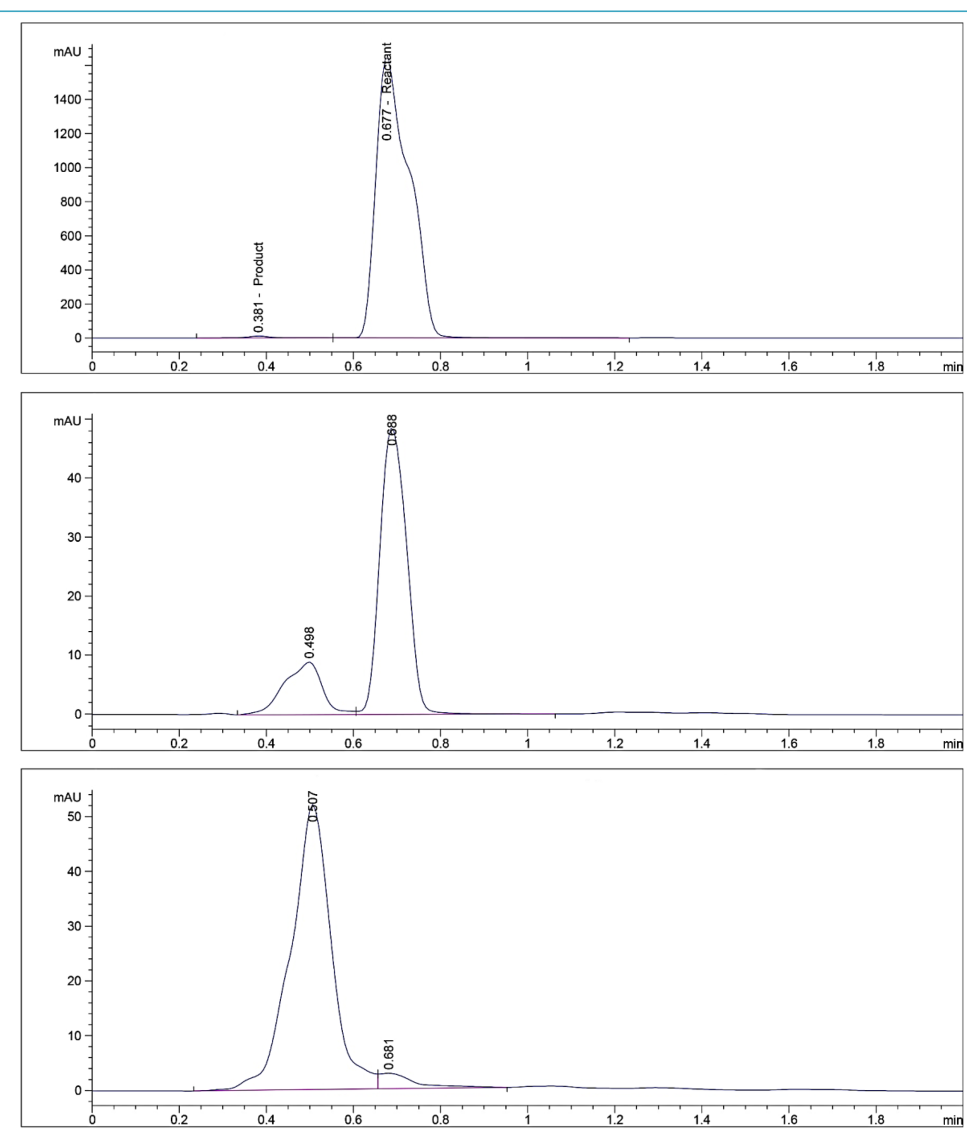


Figure 2. Monitoring of the condensation reaction by HPLC to obtain (3) at the conditions of [T=75 °C (t= 0, 6 and 28 h)].

CONCLUSION

The synthesis of (*E*)-2-(7-methoxy-1-oxo-3,4-dihydronaphthalen-2(1*H*)-ylidene)acetic acid (3) was achieved through the Knoevenagel condensation of 7-methoxy-1-tetralone with glyoxylic acid using *t*-BuOK at a temperature of 75 °C, yielding 81.40 %. The kinetic analysis allowed us to conclude that the reaction follows a pseudo-second order model. The results obtained provide valuable information about the kinetics of this reaction and establish a foundation for future studies in the synthesis and evaluation of derivatives with potential biological activity.

FUTURE WORK / REFERENCES

Investigate the activity and utility of the unsaturated acid (3).

References

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