

## KINETICS OF THE ACETYLATION OF CITRONELLOL BY ACETIC ANHYDRIDE IN GLACIAL ACETIC ACID

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(Received July 2, 1986; revised October 10, 1988)

The acetylation reaction of citronellol with acetic anhydride has been studied by two different methods and has been found to be of the first order with respect to each citronellol and acetic anhydride when the concentrations of the reactants were of the same magnitude. The energy of activation of the reaction between citronellol and acetic anhydride in glacial acetic acid was found to be 57.29 KJ/mole (G.C. method) and 57.29 KJ/mole (Titrimetric method).

*Key words:* Acetylation, Kinetics, Citronellol.

### INTRODUCTION

Terpene alcohols such as citronellol, geraniol terpineol, linalool and their esters are widely used in perfumery [1] due to their pleasant odours. These alcohols and their esters are abundantly found in nature as major constituents of a large number of essential oils [2]. These alcohols can also be synthesized and their esters can be prepared by their treatment or that of the essential oils containing these alcohols with fatty acid anhydrides at low temperatures and in the presence of a small amount of mineral acids such as hydrochloric and sulphuric acids [3].

Citronellyl acetate has been prepared from citronellol by the action of acetic anhydride at boiling temperature [4]. Mesnard *et al.* [5] have studied the acetylation of citronellol with acetic anhydride using phosphoric acid as the catalyst. *p*-Toluene sulfonic acid has also been used as acetylation catalyst [6]. Although many attempts have been made to synthesis citronellyl acetate [7-9], no work has been done to study the kinetics of this reaction. The knowledge of reaction rates and physical constants, such as activation energy, enthalpy of activation and entropy of activation is essential for the success of an industrial process as these help in the selection of the optimum conditions to obtain the best yields. The present investigations were undertaken to study the reaction rate of acetylation of citronellol by acetic anhydride and to obtain other physical constants. The results are being reported in this communication.

### EXPERIMENTAL

Citronellol was obtained from SMC Organics USA. Acetic anhydride and glacial acetic acid were of A.R. grade.

Citronellol (0.1 mole) was placed in a 100 ml three necked R.B. flask which was fitted with a mechanical stirrer and condenser and was placed in a thermostated water bath controllable to within 0.1°. Acetic anhydride (0.2 mole) and glacial acetic acid (0.1 mole) maintained at the controlled temperature were then added while stirring. The reactions were carried out at 10, 30, 50, and 70°. The progress of the reaction was followed by removing 5 ml of the reactants after each hour, quenching the reaction; diluting it to 250 ml with distilled water and titrating against 0.1N sodium hydroxide using phenolphthalein as indicator. From the titre values, the amount of unreacted acetic anhydride was calculated. The amount of the reacted alcohol was taken to be equal to that of the reacted anhydride. Immediately after titration the organic layer was separated and steam distilled. The organic layer was separated from the steam distillate and dried over anhydrous sodium sulphate. It was then gas chromatographed using a Pye Unicam 104 Gas Chromatograph fitted with an F.I.D. 25 m long 0.2 mm. id. glass capillary column coated with carbowax 20 M was used for the separation, using hydrogen gas with a flow velocity of 50 cm/sec, split ratio 1:100 as carrier gas, column temperature 100°, injector temperature 250° and detector temperature 250° were employed. Percentage ratios of citronellol and citronellyl acetate were obtained using Spectra Physics SP 4100 Computing Integrator.

### RESULTS AND DISCUSSION

The kinetic experiments by the two different methods of analysis (GC and titrimetric) were carried out at different temperatures with concentrations of citronellol (0.1M) and acetic anhydride two fold to the concentration of

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citronellol. The rate expression used for calculating the rate coefficient  $K$  was:—

$$Kt = \frac{1}{a-b} \ln \frac{b(a-x)}{a(b-x)}$$

Where  $a$  is the initial concentration of citronellol,  $b$  is the initial concentration of acetic anhydride,  $(a-x)$  is the concentration of citronellol at time  $t$  and  $(b-x)$  is the concentration of acetic anhydride at time  $t$  (Tables 1 and 2). For each run, the plots of  $\frac{1}{a-b} \ln \frac{b(a-x)}{a(b-x)}$  against time in minutes were plotted (Fig. 1 and 2). Fairly good straight lines were obtained with a slope of value being equal to the rate constant  $K$ .

Series of measurements were carried out at  $30^\circ$  at constant concentrations of acetic anhydride and citronellol. The reaction was found to be of the first order with respect to each acetic anhydride and citronellol.

**Effect of temperature.** Kinetic runs were performed in the temperature range from  $10$  to  $70^\circ$  at constant concentration of citronellol and acetic anhydride. A plot of  $\ln K$  versus  $\frac{1}{T}$  for the reaction investigated produced a straight line (Fig. 3, 4) indicating that the data closely follow the Arrhenius equation. The values of the activation energy ( $\Delta E$ ) is given in Tables 3 & 4. The enthalpy ( $\Delta H^\ddagger$ ) and entropy ( $\Delta S^\ddagger$ ) of activation for the reaction were calculated making use of the transition state theory [10] and the results

Table 1. Acetylation of citronellol with acetic anhydride in presence of acetic acid glacial using G.C. method of analysis.

Initial concentration of citronellol ( $a$ ) = 100 m. moles.  
Initial concentration of acetic anhydride ( $b$ ) = 200 m. moles.

| Temp. °C | Time (min) | X m.moles/lit. | (a-x) m.moles/lit. | (b-x) m.moles/lit. | K dm <sup>3</sup> .mol <sup>-1</sup> . S <sup>-1</sup> |
|----------|------------|----------------|--------------------|--------------------|--|
| 10°      | 60         | 4.09           | 95.91              | 195.91             | 3.52x10 <sup>-3</sup>                                  |
|          | 120        | 7.73           | 92.27              | 192.27             | 3.42x10 <sup>-3</sup>                                  |
|          | 180        | 11.20          | 88.80              | 188.80             | 3.40x10 <sup>-3</sup>                                  |
|          | 240        | 14.60          | 85.40              | 185.40             | 3.42x10 <sup>-3</sup>                                  |
|          | 300        | 16.85          | 83.15              | 183.15             | 3.22x10 <sup>-3</sup>                                  |
|          | 360        | 20.7           | 79.30              | 179.30             | 3.40x10 <sup>-3</sup>                                  |
| 30°      | 60         | 19.00          | 81.00              | 181.00             | 18.48x10 <sup>-3</sup>                                 |
|          | 120        | 33.00          | 67.00              | 167.00             | 18.35x10 <sup>-3</sup>                                 |
|          | 180        | 43.60          | 56.40              | 156.40             | 18.16x10 <sup>-3</sup>                                 |
|          | 240        | 52.60          | 47.40              | 147.40             | 18.41x10 <sup>-3</sup>                                 |
|          | 300        | 59.30          | 40.70              | 140.70             | 18.24x10 <sup>-3</sup>                                 |
|          | 360        | 65.30          | 34.70              | 134.70             | 18.58x10 <sup>-3</sup>                                 |
| 50°      | 60         | 54.40          | 45.60              | 145.60             | 78.03x10 <sup>-3</sup>                                 |
|          | 120        | 76.00          | 24.00              | 124.00             | 79.08x10 <sup>-3</sup>                                 |
|          | 180        | 86.10          | 13.90              | 113.90             | 78.33x10 <sup>-3</sup>                                 |
|          | 240        | 91.70          | 8.30               | 108.30             | 78.125x10 <sup>-3</sup>                                |
|          | 300        | 94.86          | 5.14               | 105.14             | 77.50x10 <sup>-3</sup>                                 |
|          | 360        | 97.00          | 3.00               | 103.00             | 78.97x10 <sup>-3</sup>                                 |
| 70°      | 60         | 81.30          | 18.70              | 118.70             | 192.49x10 <sup>-3</sup>                                |
|          | 120        | 94.80          | 5.20               | 105.20             | 192.84x10 <sup>-3</sup>                                |
|          | 180        | 98.40          | 1.60               | 101.60             | 192.11x10 <sup>-3</sup>                                |
|          | 240        | 99.50          | 0.50               | 100.50             | 192.09x10 <sup>-3</sup>                                |
|          | 300        | 99.85          | 0.15               | 100.15             | 193.69x10 <sup>-3</sup>                                |
|          | 360        | 99.95          | 0.05               | 100.05             | 191.89x10 <sup>-3</sup>                                |

Table 2. Acetylation of citronellol with acetic anhydride in presence of acetic acid glacial using titrimetric method of analysis.

Initial concentration of citronellol\* ( $a$ ) = 11.63 m. moles.  
Initial concentration of acetic anhydride ( $b$ ) = 23.26 m. moles.

| Temp. °C | Time (min) | X m.moles/lit. | (a-x) m.moles/lit. | (b-x) m.moles/lit. | K dm <sup>3</sup> .mol <sup>-1</sup> . S <sup>-1</sup> |
|----------|------------|----------------|--------------------|--------------------|--|
| 10°      | 60         | 0.055          | 11.575             | 23.205             | 3.40x10 <sup>-3</sup>                                  |
|          | 120        | 0.110          | 11.520             | 23.150             | 3.408x10 <sup>-3</sup>                                 |
|          | 180        | 0.166          | 11.464             | 23.094             | 3.44x10 <sup>-3</sup>                                  |
|          | 240        | 0.217          | 11.413             | 23.043             | 3.388x10 <sup>-3</sup>                                 |
|          | 300        | 0.272          | 11.358             | 22.988             | 3.410x10 <sup>-3</sup>                                 |
|          | 360        | 0.326          | 11.304             | 22.934             | 3.419x10 <sup>-3</sup>                                 |
| 30°      | 60         | 0.294          | 11.336             | 22.966             | 18.466x10 <sup>-3</sup>                                |
|          | 120        | 0.576          | 11.054             | 22.683             | 18.429x10 <sup>-3</sup>                                |
|          | 180        | 0.847          | 10.783             | 22.413             | 18.429x10 <sup>-3</sup>                                |
|          | 240        | 1.111          | 10.519             | 22.149             | 18.419x10 <sup>-3</sup>                                |
|          | 300        | 1.362          | 10.268             | 21.898             | 18.406x10 <sup>-3</sup>                                |
|          | 360        | 1.604          | 10.026             | 21.656             | 18.380x10 <sup>-3</sup>                                |
| 50°      | 60         | 1.175          | 10.455             | 22.085             | 78.348x10 <sup>-3</sup>                                |
|          | 120        | 2.182          | 9.448              | 21.078             | 78.303x10 <sup>-3</sup>                                |
|          | 180        | 3.057          | 8.573              | 20.203             | 78.373x10 <sup>-3</sup>                                |
|          | 240        | 3.817          | 7.813              | 19.443             | 78.299x10 <sup>-3</sup>                                |
|          | 300        | 4.491          | 7.139              | 18.769             | 78.385x10 <sup>-3</sup>                                |
|          | 360        | 5.084          | 6.546              | 18.176             | 78.365x10 <sup>-3</sup>                                |
| 70°      | 60         | 2.595          | 9.035              | 20.665             | 192.302x10 <sup>-3</sup>                               |
|          | 120        | 4.438          | 7.192              | 18.822             | 192.684x10 <sup>-3</sup>                               |
|          | 180        | 5.788          | 5.842              | 17.472             | 192.213x10 <sup>-3</sup>                               |
|          | 240        | 6.833          | 3.997              | 16.427             | 192.673x10 <sup>-3</sup>                               |
|          | 300        | 7.635          | 3.995              | 15.625             | 192.227x10 <sup>-3</sup>                               |
|          | 360        | 8.285          | 3.345              | 14.975             | 192.454x10 <sup>-3</sup>                               |

\*Amount citronellol and acetic anhydride in 5 ml of aliquot.

Table 3. Rate constant and activation parameters of the acetylation reaction of citronellol obtained by GC method.

| Temp °C | K dm <sup>3</sup> .mol <sup>-1</sup> .S <sup>-1</sup> (k) | $\Delta E$ K.J./mole Graphic | $\Delta E$ K.J./mole Calculated average | $\Delta G^*$ K.J./mole | $\Delta H^*$ K.J./mole | $\Delta S^*$ e.u. |
|---------|---|------------------------------|---|------------------------|------------------------|-------------------|
| 10      | 3.40x10 <sup>-3</sup>                                     | 57.29                        | 54.150                                  | 82.61                  | 52.58                  | -106.04           |
| 30      | 18.39x10 <sup>-3</sup>                                    | —                            | —                                       | 84.36                  | 52.25                  | -105.92           |
| 50      | 78.01x10 <sup>-3</sup>                                    | —                            | —                                       | 86.21                  | 51.92                  | -106.13           |
| 70      | 192.50x10 <sup>-3</sup>                                   | —                            | —                                       | 89.14                  | 51.58                  | -109.455          |

Table 4. Rate constant and activation parameters of the acetylation reaction of citronellol obtained by titrimetric method.

| Temp °C | K dm <sup>3</sup> .mol <sup>-1</sup> .S <sup>-1</sup> | $\Delta E$ K.J./mole Graphic | $\Delta E$ K.J./mole Calculated average | $\Delta G^*$ K.J./mole | $\Delta H^*$ K.J./mole | $\Delta S^*$ e.u. |
|---------|---|------------------------------|---|------------------------|------------------------|-------------------|
| 10      | 3.39x10 <sup>-3</sup>                                 | 57.29                        | 54.161                                  | 82.61                  | 52.58                  | -106.06           |
| 30      | 3.38x10 <sup>-3</sup>                                 | —                            | —                                       | 84.36                  | 52.25                  | -105.92           |
| 50      | 78.13x10 <sup>-3</sup>                                | —                            | —                                       | 86.21                  | 51.92                  | -106.12           |
| 70      | 192.13x10 <sup>-3</sup>                               | —                            | —                                       | 89.15                  | 51.58                  | -109.47           |

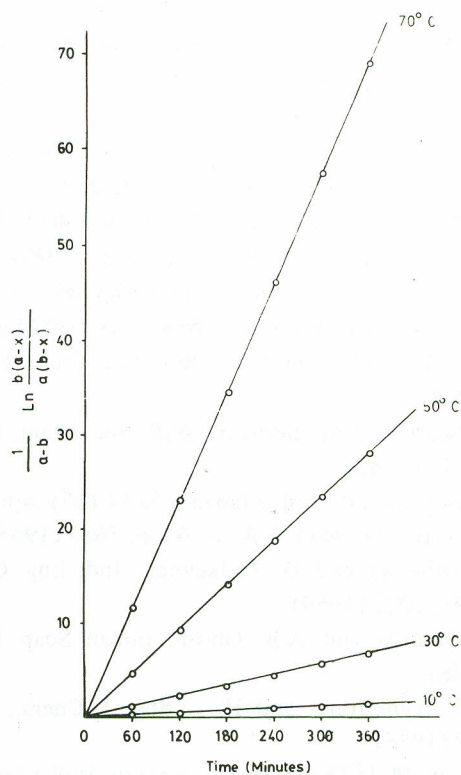


Fig. 1. Second order plots obtained by G.C. method.

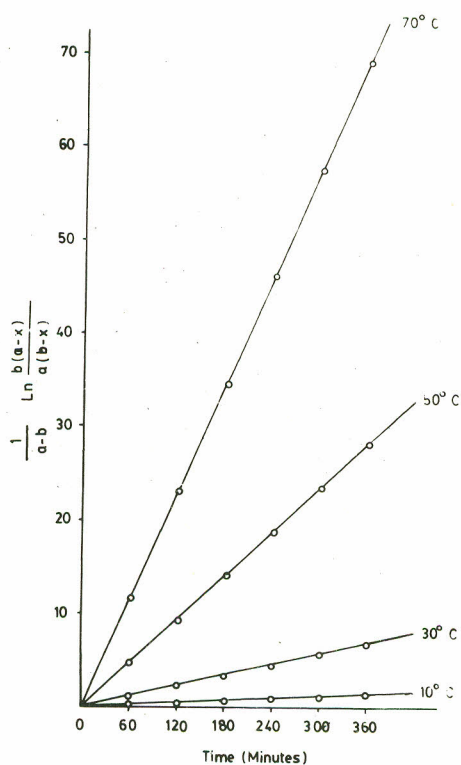


Fig. 2. Second order plots obtained by titrimetric method.

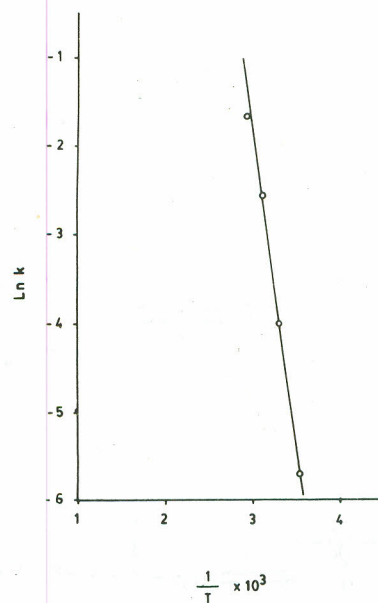


Fig. 3. Arrhenius plot of the acetylation reaction of citronellol obtained by G.C. method.

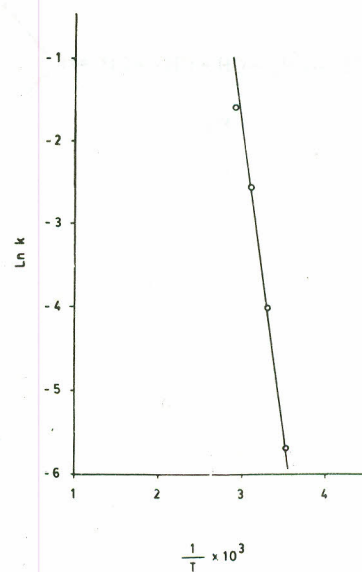
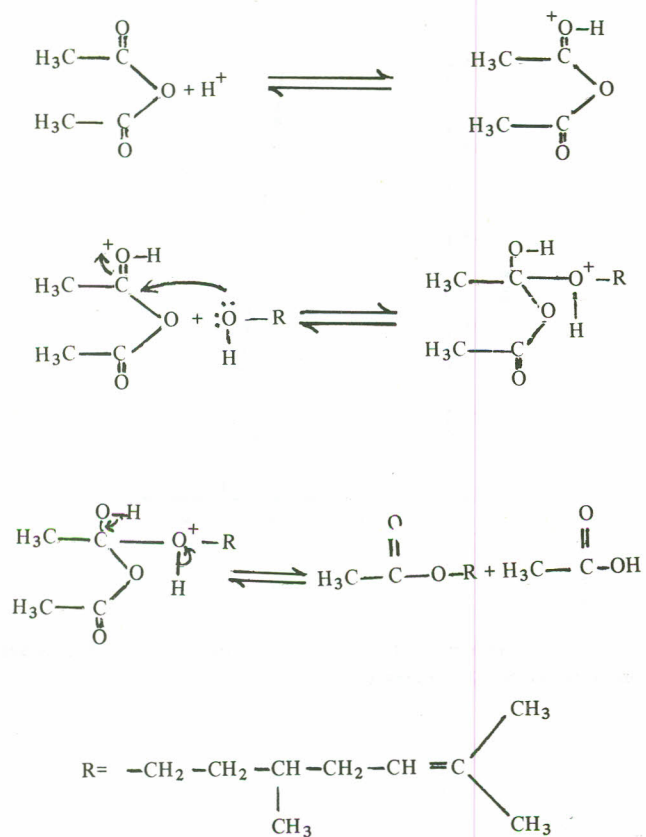


Fig. 4. Arrhenius plot of the acetylation reaction of citronellol obtained by titrimetric method.

together with the free energy of activation ( $\Delta G^*$ ) are given in Tables 3 & 4. The negative value of entropy of activation  $\Delta S^*$  obtained in this investigated system indicated that the activated complex structure is relatively more ordered than the structure of separated reactants. A comparison of the activation parameters reported here with the parameters for "conventional" acid catalysed esterification reactions [11] shows that they fall in the same range. The mechanism suggested is also similar to the "conventional" acid catalysed esterification reactions.



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