JOURNAL OF APPLIED ELECTROCHEMISTRY **23** (1993) 173–177

Mechanistic aspects and electrosynthesis of rose oxide through anodic cyclization of citronellol

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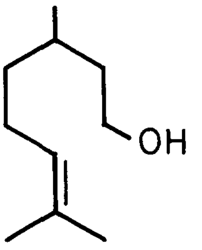
Received 30 January 1992; revised 2 June 1992

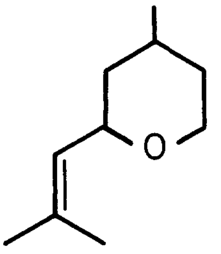
The anodic cyclization of citronellol resulting in rose oxide was investigated using 0.1 M HCl as supporting electrolyte and AN:H_20(30:70 vol %) as solvent. Depending on the switching potential used a blocking of the platinum electrode surface was observed. Pulsing of the working electrode potential between appropriate values resulted in reagent conversions with 70% yield. No secondary products were observed. The experimental results are adequately described by an EEC mechanism.

1. Introduction

The chemical oxidation of citronellol (3, 7-dimethyl-6-octen-1-ol), (**I**), an abundant natural monoterpenic alcohol, to the cyclic ether 2-(2-methyl-1-propenyl)-4-methyl-tetrahydropyrane (**II**), a minor, but important, olfactive ingredient of rose otto and geraniol oil [1–3], can be achieved by several oxidants e.g. $Pb(OAc)_4$ [4]. **II** is commercially known as rose oxide.



I



II

The commercial importance of rose oxide (**II**) can be evaluated from the significant number of existing patents describing its synthesis using citronellol (**I**) as starting material. (A list of patents is provided in [5]). Early attempts by normal organic synthetic routes, besides involving several intermediate steps and showing modest yields, frequently resulted, as a consequence of oxidative fragmentation, in a mixture of products, for example aldehydes, ketones, aliphatic ethers, etc. Eschinasi [5], using citronellyl acetate as starting material, was the first to report a more practical and economic synthetic route resulting in **II** with an overall yield of approximately 70%. The synthetic route, however, still involves several intermediate steps.

As far as is known, Shono *et al.* [6] were the first to propose an electrochemical synthetic route for **II** through anodic cyclization of **I**. A 26% yield, together with a mixture of subproducts, was obtained. Suzukano *et al.* [7] took a patent on an electrochemical synthesis of **II** showing an overall yield of 45.2%. Gora *et al.* [8] were able to convert **I** to **II**, electrolysing for 20 h, using a potential between 1.4–2.2 V, a mixture of 1 mol **I** + 10–20 moles AN + 0.1–0.5 M TEAP, obtaining a 52% yield. A mixed electrochemical–classical organic synthetic route, with an overall yield of 80%, was proposed by Torii *et al.* [9]. Basically their procedure consisted in an electrochemical oxyselenenylation–deselenenylation sequence followed by a Lewis acid catalyzed cyclization of the intermediate. Recently, Smigielski and Gora [10] were able to cyclize **I**, obtaining **II** with a 32.5% yield, using a non-aqueous solvent and a DSA® as the working electrode.

In view of the importance of the anodic cyclization, a clean single step synthetic route, it was decided to investigate the electrochemical procedure in order to increase the yield of **II** obtained.

2. Experimental details

Citronellol (Dragoco, S.P., Brazil) was used as received. Its purity, checked by GC, was > 99.5%. A stock solution of appropriate concentration in acetonitrile (Uvasol-Merck), AN, was prepared by direct weighing of the appropriate mass. Working solutions in HCl 0.1 M using AN:H_20 (30:70; v/v) as the solvent were prepared by mixing appropriate volumes of the **I** stock solution, H_2O, HCl 1 M (stock) and pure AN. AN was used as received.

A PAR model 173 potentiostat equipped with a model 175 universal programmer was used throughout. For lower than 500 mV s^{-1} sweep rates the output signal was recorded with a model HP7045 XY recorder. A PAR model 4102 signal recorder was used for higher sweep rates. A PAR model 179 digital coulometer was used during the controlled potential coulometric experiments. All potentials were checked

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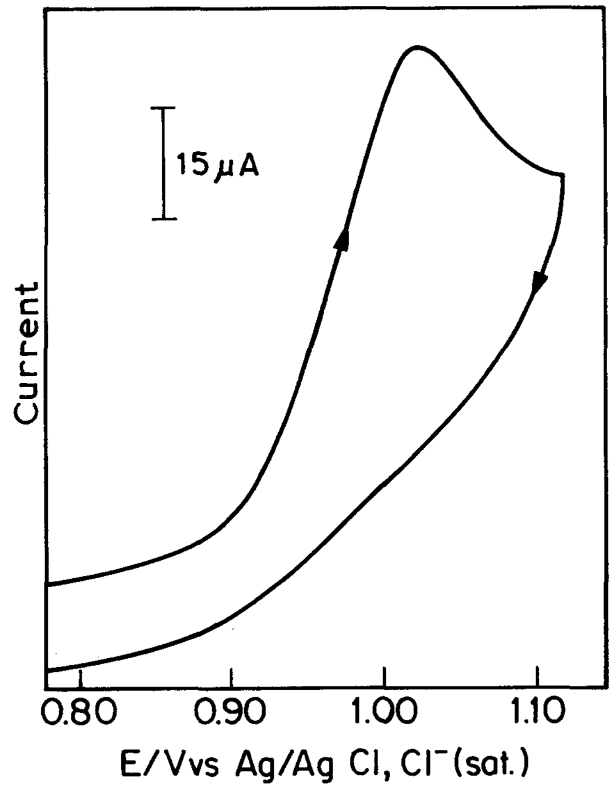


Fig. 1. Cyclic voltammogram of 0.746 mM citronellol in 0.1 M HCl. Solvent: H_2O:AN (70:30 v/v); v = 100 mV s^{-1}. Working electrode: Pt-disc.

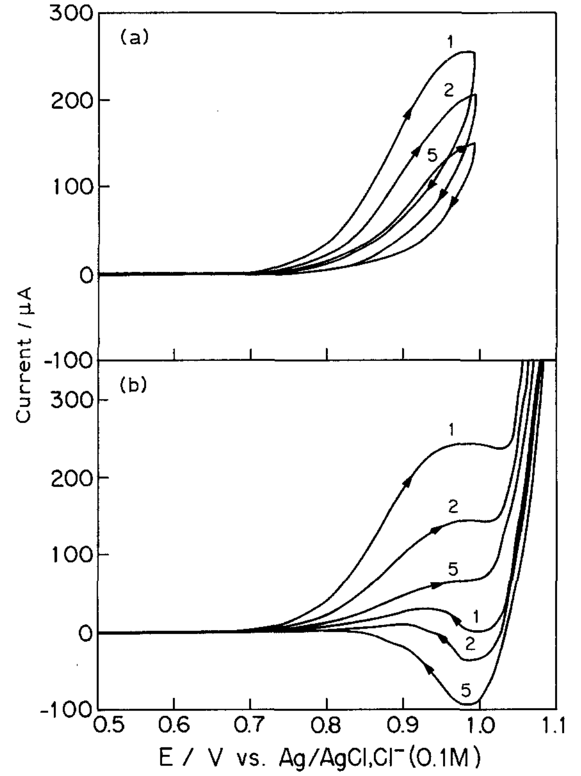


Fig. 2. Effect of E_λ on the cyclic voltammetric behaviour during continuous potential cycling. (a) E_λ = 1.00 V (b) E_λ = 1.08 V. 3.88 mM citronellol. Pt-disc.

with a Keithley model 172A multimeter. NMR ^1H spectra were recorded on a Varian model EM-360 spectrometer while i.r. spectra were obtained on a Perkin–Elmer model 257 spectrometer.

The electrodes used during the electrochemical studies were: Pt-disc (Beckman 39273) or Pt-gauze type (Beckman 39009) as working electrode; a Pt-wire (Metrohm EA202) as auxiliary electrode and a Ag/AgCl, Cl^- (sat.) or Cl^- (0.1 M) as reference electrode, with the exception of the chronoamperometric study, were a silver wire immersed in a 0.1 M NaCl, separated from the solution by a Luggin capillary, was used as a reference electrode.

The pretreatment of the working electrode was started by polishing the electrode with α-Al_2O_3(PAR–Raibrite A) followed by an electrochemical cleaning procedure consisting of cycling the potential continuously between +0.55 V and +1.1 V until a low, flat background current was obtained. This α-Al_2O_3 polishing step was omitted in the case of the Pt-gauze working electrode. The experimental behaviour of the Pt-disc electrode was checked employing the $Fe(CN)_6^{-3}$ system. An electrochemical area of 0.23 cm^2, very close to the geometric area, was found.

3. Results and discussion

3.1. *Cyclic voltammetry*

A representative voltammogram of the cyclic voltammetric behaviour of **I** in 0.1 M HCl(H_2O:AN 70:30 v/v) is shown in Fig. 1. For all sweep rates, v, investigated the voltammogram is characterized by a single anodic peak, close to the discharge of the supporting electrolyte, no cathodic peak being obtained. At the higher sweep rates the anodic peak strongly overlaps with the background current imposing a limit of 2 V s^{-1} to the experimentally possible sweep rate.

The switching potential, E_λ, had a marked influence on the cyclic voltammetric behaviour observed. This study was executed at a 3.88 mM **I** concentration where, according to the i_p against [**I**] plot, the deviation from linearity is already significant (see Fig. 3). Figure 2 shows the influence of two different E_λ values as a function of the number of continuous cycles. In Fig. 2(a) E_λ was chosen at +1.00 V, a potential localized at the beginning of the potential region known as the 'Pt-oxide' region. In contrast, in Fig. 2(b), the switching potential was chosen to be +1.08 V, a value which significantly coincides with the Pt-oxide region. In the first case the peak current decays to 80% and 60% of the initial current, after the second and fifth cycle, respectively. Choosing a more anodic E_λ value the rate of current decay is much faster. So with E_λ = 1.08 V (see Fig. 2b) currents after the second and fifth cycles are 60% and 25% respectively of the initial current. If a sufficiently anodic value of E_λ is chosen almost no current is observed after the second cycle. If after a single cycle the platinum electrode is cleaned (see experimental section) the observed currents are reproducible.

It is known from the literature that the sequence of anodic peaks, observed in the more positive potential region of the cyclic voltammogram of a polycrystaline platinum electrode, is due to the oxidation of the platinum surface, resulting in its covering by a layer of

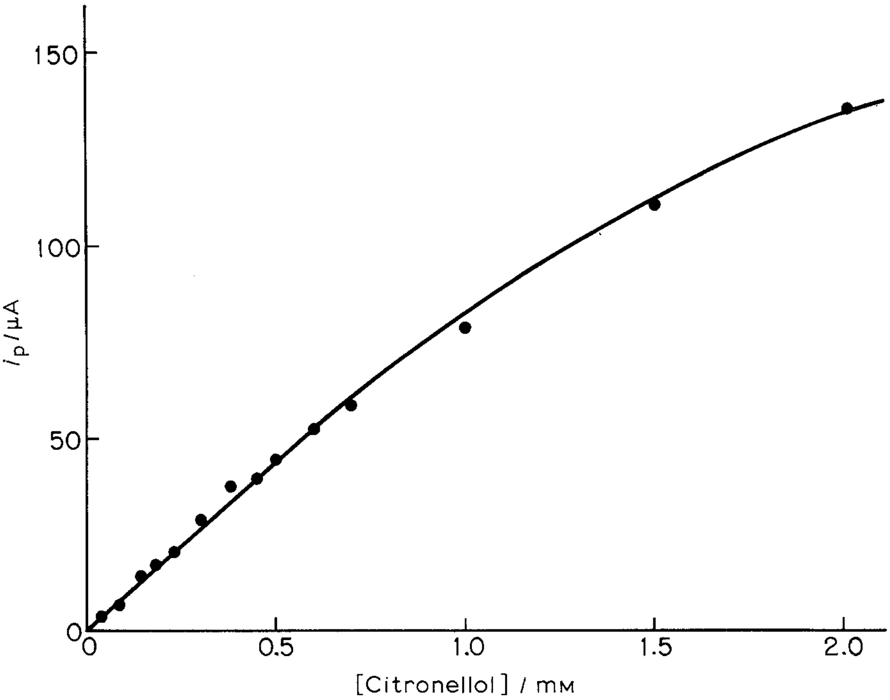


Fig. 3. Peak current as a function of citronellol concentration in 0.1 M HCl. Solvent: H_2O:AN (70:30 v/v). v = 100 mV s^{-1}. Pt-disc.

oxygen containing Pt-species, for example PtO, PtOOH, PtO_2, etc. [11, 12]. So the behaviour of the electrode in the presence of **I**, on continuous cycling of the potential, can be explained as a blocking of the active sites by **I** or a product. In view of this result care was taken to clean the surface before the recording of each voltammogram.

The influence of the concentration on the peak current, i_p, and peak potential, E_p, was investigated as a function of the concentration of **I** covering the interval between 0.04 and 2.0 mM. A linear dependence between i_p and the concentration was observed up to approximately 0.75 mM, showing the current to be diffusion controlled at the lower concentrations (Fig. 3). For the higher concentrations of **I**, i_p levelled off. Theoretically, the behaviour at the higher CIT concentrations of the i_p against concentration graph, may be explained as a consequence of dimerization of the CIT-radical, formed after the first electron removal. Dimerization, being governed by second order kinetics, is favoured with increasing CIT concentration, explaining the negative deviations of the current from the expected value. However, the results of the analysis of the reaction products, isolated after exhaustive electrolysis, did not reveal the occurrence of a dimer. So in case the CIT-radical dimerization reaction really occurs its contribution to the electrode process must be considered negligible. We therefore prefer to attribute the levelling off of i_p shown in Fig. 3 to be a consequence of surface blocking at the higher citronellol concentrations. Using the Randles–Sevcik equation [13, 14] a value of $2.52 \times 10^{-6} cm^2 s^{-1}$ for the diffusion coefficient was obtained from the slope of the linear part of the i_p against concentration graph. The experimental results also suggest E_p to be, within 10 mV, independent of concentration. The investigation of the influence of the sweep rate resulted in a linear dependency of i_p on $v^{1/2}$, $i_p/v^{1/2}$ being almost independent of v. A value of $2.24 \times 10^{-6} cm^2 s^{-1}$ for the diffusion coefficient was obtained, in good agreement with the value obtained from the i_p against concentration relationship. E_p had a linear dependence on log v, showing an anodic displacement of 34 mV per decade sweep rate increase.

Based on the diagnostic tests proposed by Nicholson and Shain [15] and Nadjo and Saveant [16] for an EEC mechanism, our results suggest that citronellol oxidation occurs through relatively fast electron transfer steps followed by a chemical step having a very large rate constant. Because of the limited sweep rates ($\leqslant 2 V s^{-1}$) experimentally accessible no reverse peak was observed. Thus the present data are confined to the pure kinetic zone not permitting kinetic data to be obtained [15, 16].

3.2. *Double potential step chronoamperometry*

Since the highest experimental sweep rate was limited to $2 V s^{-1}$ it was decided to explore the chronoamperometric technique using lower time window values. The initial potential was stepped from +0.600 V, where no oxidation occurs, to a value of +1.050 V, where the oxidation of **I** is diffusion controlled, and back to +0.600 V. Pulse durations in the time interval between 1 ms and 10 s were used. Concentration was kept constant at 0.74 mM.

While, for all pulse durations investigated, significant oxidation currents were observed, no cathodic current was observed even at the shortest pulse durations investigated, confirming that the rate constant of the following chemical reaction is very fast ($k_c > 1000 s^{-1}$). For all pulse durations investigated the i against $t^{-1/2}$ plot (Fig. 4) is linear confirming that currents are diffusion controlled. From the experimental results a value of $4.14 \times 10^{-6} cm^2 s^{-1}$ for

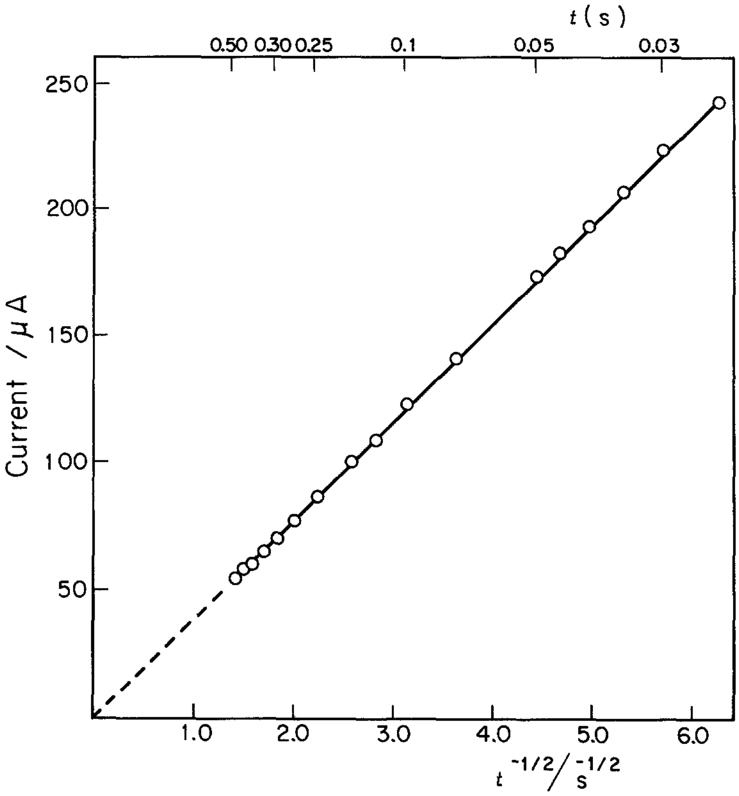


Fig. 4. Current as a function of $t^{-1/2}$. $\theta = 0.5$ s. 0.742 mM citronellol in 0.1 M HCl. Solvent: H_2O : AN (70 : 30 v/v). Pt-disc.

D_I was calculated, showing good agreement with the value obtained from the cyclic voltammetric results.

3.3 *Controlled potential coulometry (CPC)*

A series of controlled potential coulometry (CPC) experiments of 2.29 mmol of **I**, contained in 40 ml of supporting electrolyte, were executed as a function of the potential applied, E_{ap}, to the working electrode. The E_{ap} examined, changed in 10 mV steps, was confined to the +1.03 to +1.08 V potential interval. A value of 2, independent of the E_{ap} used, was found for the number of electrons transferred, n_{ap}, in the $E_{ap} \leqslant +1.05$ V region. For $E_{ap} \geqslant +1.07$ V, the n_{ap} values were found to increase as a function of the duration of the experiments. The constant experimental n_{ap} value of 2, found for $E_{ap} \leqslant +1.05$ V, suggests the oxidation of **I** to occur without the competition of a chemical reaction which deactivates intermediates (e.g. the dimerization of the radical formed after the first electron removal), otherwise n_{ap} values deviating from 2 should have been obtained. The results obtained in the $E_{ap} \geqslant +1.07$ V region, where the experimental n_{ap} increases as a function of time and reaches values larger than 2, can be explained as the result of the contribution to the recorded total charge of the formation of platinum oxides [11, 12].

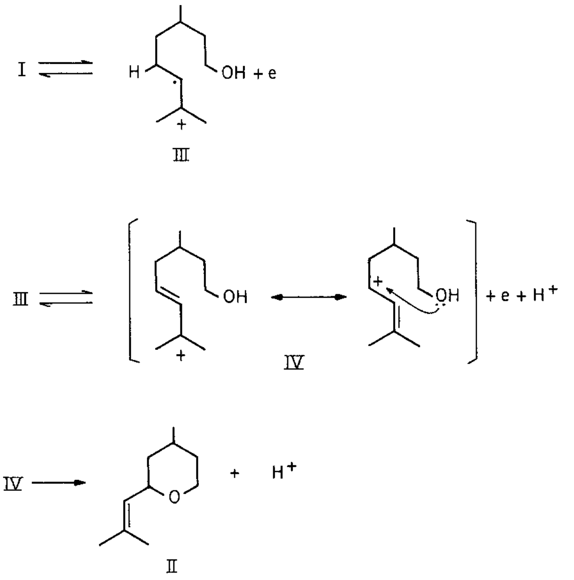
3.4 *Controlled potential electrolysis (CPE)*

All experiments were conducted using a gauze type platinum electrode, electrolyzing 0.15 g of **I** contained in 80 ml of the supporting electrolyte solvent mixture. Initially electrolysis was done using a fixed value of +1.05 V for the working potential. Under these experimental conditions the current dropped rapidly to a low level and analysis of the reaction mixture established that almost no conversion of **I** occurred. This behaviour can be understood in the light of the blocking effect observed during the CV investigation (see Section 3.1). Thus a series of experiments were conducted reactivating the electrode surface by pulsing the working potential applied to the platinum electrode between +1.05 V (where **I** oxidation occurs) and +0.55 V (potential localized in the double layer region of the platinum cyclic voltammogram where the oxide species formed during the anodic cycle are reduced). Five seconds at +1.05 V followed by 1 s at +0.55 V was found to be effective in obtaining an excellent conversion of **I** to **II**. Under these experimental conditions an initial electrolysis current of approximately 50 mA was observed. The electrolysis was interrupted after 5 h when the current had fallen to 0.7 mA. At the end of the electrolysis a total anodic charge of 148 C had passed corresponding to 80% of the theoretical charge of 184 C, assuming 2 faraday mol^{-1}, necessary for complete conversion of **I** in **II**.

After neutralization of the reaction mixture and extraction of the organic material this was analysed by gas chromatography and found to be composed of 80% of **II** and 20% of the starting material. The organic product mixture was separated by silica-gel plate chromatography using CH_2Cl_2:EtOH, 9:1, as eluent and the individual components were identified by i.r. and NMR^1H by comparison with literature data published by Seidel *et al.* [17]. A 70% yield, expressed as purified **II**, was obtained. In view of this quite reasonable yield, at least for the concentration levels used in these experiments, it may be concluded that, even at the higher concentration levels (compared to the CPC investigation) competing chemical steps capable of drastically reducing the yield do not occur to any significant extent.

4. Conclusions

The mechanism which best represents the experimental data is an EEC one, the final chemical step being very fast.



The fact that the working potential has to be pulsed to avoid the observed blocking of the electrode surface is a disadvantage. However, the fact that a very simple reaction mixture is used, giving a reasonable yield without the production to any significant extent of secondary reaction products, recommends the anodic cyclization route as a good alternative.

Currently work is under way to investigate whether adatom modified platinum electrodes are able to convert **I** into **II** without suffering from the blocking effect shown by polycrystalline platinum electrodes.

Acknowledgements

The authors wish to aknowledge financial support received from the FAPESP Foundation (Fundação de Amparo a Pesquisa do Estado de São Paulo, S.P., Brazil) and to Prof. Luiz Alberto Avaca (IFQSC/USP, S.P., Brazil) for valuable suggestions.

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