E2-25: Electrochemical modification of citral

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Citral belongs to the class of compounds known as terpenes whose structures are labile to common chemical reagents such as acids, alkali and redox agents. The chemical modification of these compounds is therefore not straight forward. On the other hand, electrochemical modification has become one of the most successful routes of organic synthesis. This is particularly useful as the necessary reagents are synthesised *in situ* at low concentrations and the reaction is forced under diffusion controlled conditions at a catalytic surface. This paper is based on the electrochemical modification of citral under potentiostatic conditions in acetonitrile medium. Activation overpotential values of citral reduction were obtained from cyclic voltametry.

Electrochemical studies of citral were performed in a one-compartment cell consisting of a Pt-disc (surface area 3.5 x $10^{-5}m^2$) working electrode, a saturated calomel reference electrode (SCE) and a Pt-gauze auxiliary electrode. The reference electrode was placed very close to the working electrode with the help of a Lugguin capillary in order to minimise the Ohmic potential drop through the solution. All the potentials quoted are with respect to SCE. The electrolyte used was a deoxygenated solution containing 0.1 mol dm^{-3} tetrabuty1- ammonium tetrafluoroborate (TBATFB) and the required amount of citral (usually in the milliomolar range). The cell also had an inert gas (O_2 free N_2) blanket to prevent diffusion of O_2 back into the solution. In a typical experiment, the required quantity of citral was injected into the solution and the cyclic voltamogram (CV) of the Pt electrode in this solution was recorded. The system was then subjected to the constant potential electrolysis at its reduction peak potential. The elecctroysis was followed by chromoamperometry and TLC.

The products formed were separated from the reaction mixture by extracting the former into a non-polar organic solvent (n-hexane or carbon tetrachloride) and evaporating the solvent under reduced pressure. The products were characterised by IR and ^{1}H-NMR spectroscopic methods.

The CV (range:-2.O to +2.8V) had a characteristic cathodic peak centred at -0.37 V whose height increased proportionately with the citral concentration. It is, therefore, clear that this peak is due to the reduction of citral. Potentiostatic electrolysis of the system at this value resulted in a mixture of products as revealed by its TLC. The addition of $HClO_4$ resulted in a significant enhancement of the peak current and a considerable cathodic shift of the peak potential. However, this peak current was found to be independent of the citral concentration but linearly proportional to the concentration of $HClO_4$. Repeating the CV in a range where the overvoltage was insufficient for PtO formation (i.e. below 0.0V) did not show any reduction peak in this range. The peak is, therefore, due to the reduction of PtO formed on the surface at high potentials.

In the presence of $HClO_4$, there appears another peak centred at -1.25 V whose height was found to be independent of the acid concentration but linearly proportional to the concentration of citral. This peak was not found in the absence of $HClO_4$. Constant potential electrolysis of this system at this peak potential produced a reaction mixture which gave a single spot in its TLC whose R_f is 0.44 (with ethyl ethanoate as the eluent). This R_f value is much lower then that of citral (R_f=0.66 with the same solvent). The product was isolated as a yellow liquid with a characteristic odour in 97% yield. IR spectrum of citral showed bands centred at 1650 cm^{-1} (C=C), 1670 cm^{-1} (C=O), 2995 cm^{-1} (C-H of CHO) which were absent in the IR spectrum of the product. The product showed an IR absorption in the range 3250-3550 cm^{-1} indicating the presence of -OH group. ^{1}H-NMR spectrum of the product is as follows:-

d(CCl_4) 1.1(9H, d J=3 Hz, 3 methyl protons), 1.6(10H, m, 4 CH_2 and 2 C-H protons), 2.5 (1H, broad s, D_2O exchangeable, O-H proton), 3.3(2H,t,J=4Hz,CH_2-O protons)
All these data clearly show that the product is 3,7-dimethyloctanol.

The potentiostatic electrolysis of citral on a Pt surface in an acetonitrile medium containing TBATFB and $HClO_4$ results in the formation of 3,7-dimethylocatanol in 97% yield. Comparison of this result with those in the literature clearly shows that the nature of the electrode/solution interface plays an important role in determining the path of an electrochemical process.