THE ELECTROCHEMICAL BEHAVIOUR OF CITRAL

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The polarographic reduction of citral was investigated in a three electrode cell at 27 ± 1°C. The electrolyte was 0.1 M buffer of various pH values (ranging from 2–10) in water-25% ethanol mixtures. The reference electrode was a saturated calomel electrode.

There was a well defined diffusion wave. The current was not everywhere proportional to the square root of the head of mercury, showing that the reaction was not reversible. A plot of E vs $\ln \frac{i - i}{i}$ gave a value of 0.6 for αn ; for α approximately $\frac{1}{2}$ this would give $n = 1$. The half-wave potential increases with pH up to about pH = 3.5, is then constant till about pH = 7 and again shows a slow increase.

Cyclic voltammetry on the hanging mercury drop confirms the irreversibility of the electrode reaction. Plots of $i_p/v^{\frac{1}{2}}$ vs v do not give an unambiguous clue to the mechanism but is consistent witha mechanism of the type

$$R + H^+ \leftrightharpoons RH^+$$

$$RH^+ + e \longrightarrow RH.$$

Large scale electrolysis, both potentiostatic and galvanostatic, gave a mixture of products in which the carbonyl group and one of the double bonds had been reduced. NMR, IR and MS data suggest that one of the major products is the coupling product of free radicals produced in the initial charge transfer step.