Electrode Kinetics of Electroreduction of Peracetic Acid at Gold Electrode in Aqueous Media

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Introduction– Organic peroxides have been used in a multifarious range of industries, typically as oxidizing agents in organic syntheses, catalysts in polymerization reactions, bleaching reagents in textile and paper industries and disinfectants in food industries. Of these peroxides, H_2O_2 has attracted a special interest as an intermediate product in the electroreduction of oxygen. The previous electrochemical studies on other peroxides have been mainly restricted to their polarographic behavior[1]. The present study is devoted for studying the mechanism and kinetics of electroreduction of peracetic acid (PAA), which always coexists with H_2O_2[2], in aqueous media. Cyclic voltammetric (CV), hydrodynamic voltammetric (HV) and hydrodynamic chronocoulometric (HCC) measurements at Au electrode have been carried out for this purpose.

Experimental– CV, HV and HCC measurements have been carried out using a BAS 100 B/W electrochemical analyzer. Au electrode was polished mechanically using alumina powder and then electrochemically by repeating the potential scan in the range of -0.2 to 1.5 V versus Ag/AgCl (NaCl sat.) until the CV characteristic for a clean Au electrode was obtained.

Results and Discussion- Fig. 1 shows the typical HCC curves obtained for the reduction of PAA at pH 4.7. The potential was stepped from 0.6 V to – 0.4 V. A linear regression for each curve was carried out over the electrolysis time domain between 1.2 and 1.5 s, where a steady state current condition was reached. From these results, the number (*n*) of electrons involved in the overall electrode reaction and the diffusion coefficient of PAA were simultaneously determined. The kinetic parameters including the Tafel slope, the standard rate constant (k^o), the electrochemical reaction-order (*m*) and the product (αn_a) of the transfer coefficient and the number of electrons involved in the rate-determining step were determined in the pH range of 3-6. Based on the experimental results, an EE mechanism which involves the formation of either hydroxyl or acetate radical as a probable intermediate is proposed.

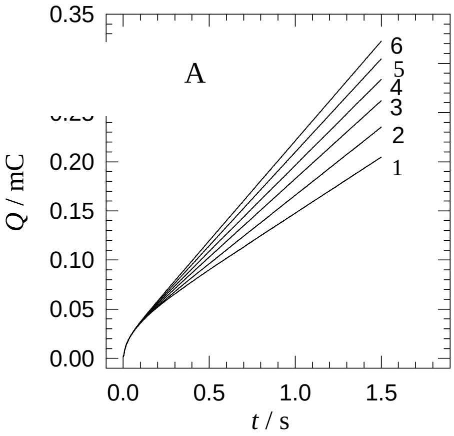

Figure 1. Typical hydrodynamic chronocoulometric data for the reduction of 5.5 mM PAA at a rotating Au disk electrode (ϕ = 2.0 mm) in N_2-saturated acetate buffer solution of pH 4.7 containing 0.1 M Na_2SO_4. Electrode rotation rate: (1) 400, (2) 600, (3) 800, (4) 1000, (5) 1200 and (6) 1400 rpm. The potential of the working electrode was stepped from 0.6 to – 0.4 V.

References

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