m*l* of ether. The mixture was then hydrolyzed with water, followed by oxidation with alkaline hydrogen peroxide in the usual manner[11]. The mixture was saturated with potassium carbonate and the separated organic layer after drying with anhydrous magnesium sulfate was subjected to fractional distillation. The yield of crude 2-octanol was 85% (5.5g). The product was further purified through 10% CW 20M column and the purity of reduction product was confirmed by an analytical GLC. The optical rotation of 2-octanol was $[\alpha]_D^{22}$ $-3.02°$ (neat), 30.5% ee in R[5].

The collected portion of 1,2-epoxyoctane was reduced to 2-octanol with excess $LiAlH_4$ at 0°C, and then the mixture was treated with 1.5 m*l* of 10 M $BH_3.SMe_2$ to hydroborate excess α-pinene. The mixture was then hydrolyzed, followed by oxidation with alkaline hydrogen peroxide. The separated alcohol product was purified as described above to give a pure 2-octanol $[\alpha]_D^{22}$ $+2.95°$ (neat), 29.8% ee in S[5].

Asymmetric Reduction of Episulfides with (−)-Diisopinocampheylborane-Lithium Chloride (1:0.1). The procedure for the reaction of episulfides with this system is exactly same as the case of reaction of epoxides described above. In the case of 1-butene sulfide, the optical rotation of the pure reduction product (2-butanethiol) was $[\alpha]_D^{22}$ $-3.04°$ (neat), 17.7% ee in R[8].

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An Electrochemical Study on the Formation and Growth of Conducting Polyaniline

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In 1862 Letheby[1] reported that a dark green precipitate could be obtained on a platinum electrode when aniline was electrochemically oxidized in aqueous sulfuric acid solutions. Subsequent investigators[2-5] verified this result and called the precipitate "aniline black", and attempted a larger scale oxidation until about 1950. Mohilner, Adams, and Argersinger[6] proposed a reaction scheme, on the basis of polarization curves, which seems to be generally accepted at the present time. They suggested that the oxidation process proceeds via head-to-tail coupling of the cation radical of aniline. An ESR spectrum that has given ample evidence for cation radical intermediates, was reported(4) in an aprotic solvent. However, it was not observed in aqueous solution. Adams group[4] proposed in the case of N-substituted anilines that a dication intermediate undergoes nucleophilic attack by the parent amine and results in the tail-to-tail coupling.

Under certain conditions the peak currents in the cyclic voltammograms were observed to be increasing with the number of cycles. In view of recent studies on conducting polymers[7-12], it is interesting to note that these increases may be interpreted as an evidence for polymer growth of conducting character.

In this communication electrochemically measured data are presented on the formation and growth of conducting polyaniline. The data were obtained from cyclic voltammetry and kinetic measurements of electrochemical oxidation of aniline on platinum electrodes in aqueous sulfuric acid solutions. The potentials given here are referred to a saturated calomel electrode(SCE).

Figure 1 illustrates typical cyclic voltammograms(CVs) for the growth of polianiline(PANI) films on the platinum electrode in aqueous 1.0M H_2SO_4 solution. From about 0.85V *vs* SCE in the first scan, an anodic rising current associated with the oxidation of aniline is observed. However,

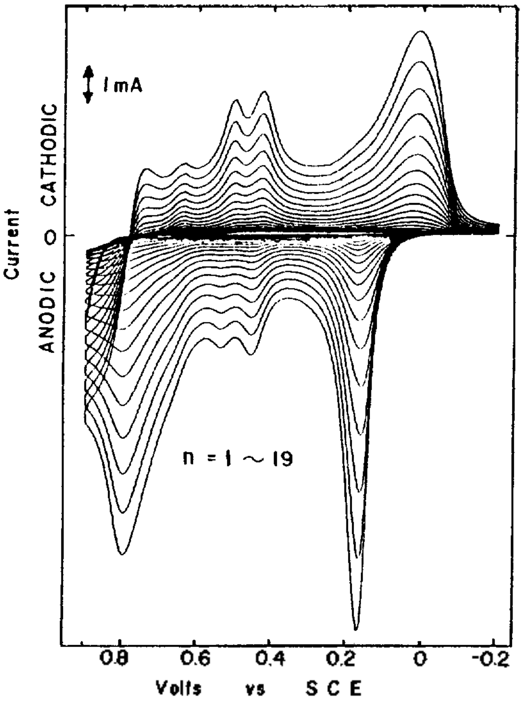


Figure 1. Typical growth curves for polyaniline in 1.0M H_2SO_4. (ANI) = 0.10M. Potential range is -0.2 to 0.9 Volts vs SCE with scan rate of 100 mV/sec. The cycle numbers(n) are 1 to 19, from bottom to top, respectively.

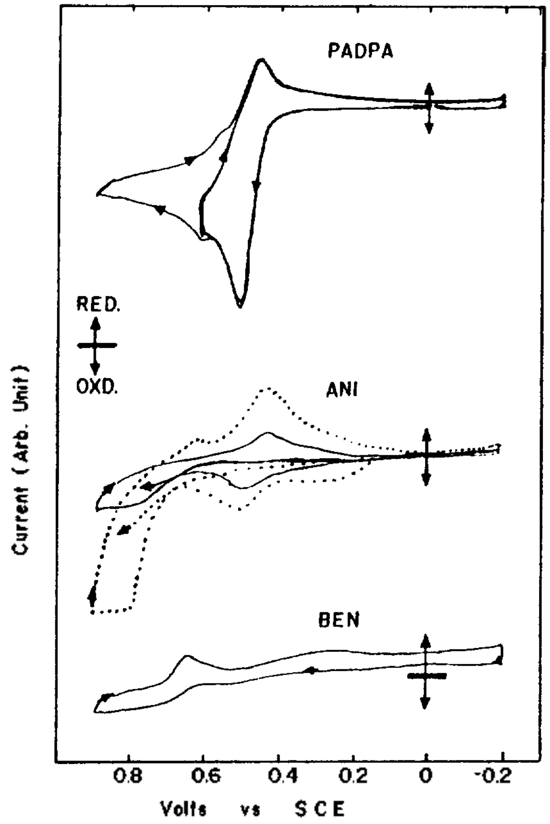


Figure 2. Typical cyclic voltammograms for p-aminodiphenyl amine (PADPA, 0.01M), aniline (ANI, 0.01M (dashed line) and 0.001M (solid line), and benzidine (BEN, saturated concentration) in 1.0M H_2SO_4.

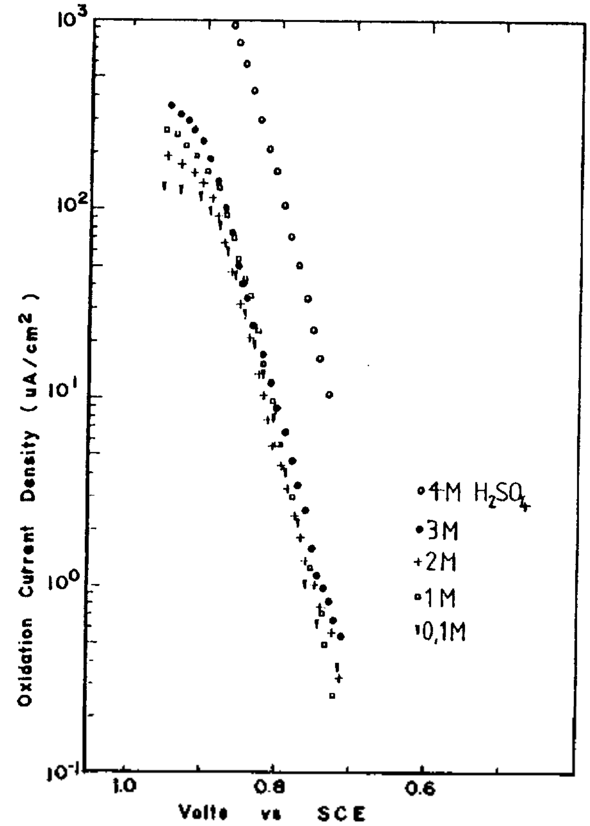
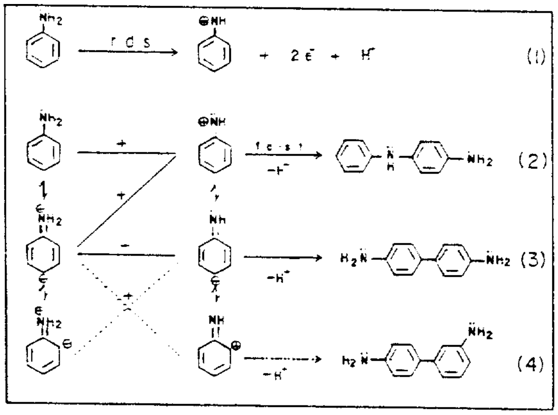


Figure 3. Anodic steady state polarization curves for 0.01M aniline in aqueous H_2SO_4 solutions.

from the second scan, the anodic peaks appeared and increased at less positive potentials. Furthermore, the CV peaks corresponding to the polymer growth begin to appear and increase, even when the switching potential for the potential sweeping was below the oxidation-peak of about 0.80 V. This indicates that the oxidation process taking place at or below this peak is responsible for the polymer growth.

It was previously reported[13] that the cathodic peaks at 0.20 and 0.75V, and the anodic peaks at 0.16 and 0.80V on the 19th scan are presumably due to the reduction and oxidation of polyaniline-film, respectively. However, the other peaks were not confirmed. Shown in Figure 2 are typical CVs for p-aminodiphenylamine(PADPA), aniline and benzidine (BEN) on platinum electrode in 1.0M H_2SO_4. The redox peak potentials of PADPA and the reduction peak of BEN of Figure 2 are very close to 0.43, 0.54 and 0.64V of Figure 1, respectively. It seems that PADPA and BEN may be an intermediate or a side-product in the oxidation process of aniline, or may be degradation products of polyaniline.

The steady state polarization curves for the oxidation of aniline under various concentrations of H_2SO_4 are shown in Figure 3. Tafel slopes were 60mV at higher polarization region, and 80mV at lower. The pH dependance was absent between the H_2SO_4 of 0.1 and 3.0M. When two parallel reactions with different Tafel slopes ocurr, the steady state polarization curves for the two reactions will cross at a point and the overall current is dominated by the higher current[14], the higher current at a given potential will be measured. Thus, the curves in Figure 3 may be taken as supporting evidence for the competitive reactions between the oxidation of aniline



Scheme 1. Electrochemical oxidation mechanism of aniline.

and PANI-film.

Based on the above argument, the following Scheme 1 is assumed as the mechanism of oxidation of aniline at higher polarization.

The pKa of anilinium ion was reported to be 4.60[15]. Therefore, in the bulk solutions tested here anilinium ion is probably dominant over neutral aniline. However, when the oxidation potential is applied, owing to the accumulation of positive charge on the pt-electrode the neutral aniline may exist within the electric double layer possibly attached to the electrode.

If the reaction (1) is the rate-determining step, the following relation is obtained:

$$i = 2Fk(ANI)\exp(2\beta FE/RT)$$

where β is the symmetry factor of the free energy profile of the reaction (1) and F is the Faraday constant. Thus, the logarithmic current is at 298 deg.K,

$$\log i = \log(\mathrm{const.}) + \log(ANI) + 2\beta E/0.0592.$$

If β is considered to be abouy 1/2 as usual, the Tafel slope will be 60 mV and the pH-dependance will be absent. The observed values at higher polarization of Figure 3 are in good agreement with this prediction within the experimental error.

If the PANI-film grows by the competitive oxidations of aniline and PANI at the region of higher polarization overall reaction rate will be dominated by the oxidation of aniline, whereas at lower polarization the oxidation of PANI-film will control the rate. Since the oxidation of aniline is assumed to be the rate determinig step at higher polarization, the kinetic parameters will be very similar to that of Scheme 1 as metioned above.

On the contrary, the overall reaction rate at the lower polarization region is controlled by the oxidation of PANI film. Thus, the current is:

$$i = nFk(PANI)\exp(\beta nFE/RT).$$

If β is assumed to be about 1/2, the Tafel slope from the above equation will be 120/n mV, which is not close to the observed 80 mV in any case of n-value. However, the oxidation of PANI seems to be quasi-reversible from Figure 1. Therefore, the symmetry factor, β will be smaller than 1/2.

When the PANI-film is oxidized via the rate determining step of two-electron transfer, the symmetry factor, β is calculated to be 0.38 from the observed Tafel slope, 80 mV. Thus, it seems that the oxidation of PANI-film is also occurring by two-electron transfer per an electroactive site.

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