

CHAPTER 4

CONCLUSION

The electrochemical behavior of five ketone and eight quinones were performed by cyclic voltammetry in CH_3CN solution at glassy carbon electrode. All the experiment found that peak of blank solution does not appear, indicating that there is not significant impurities and peak of oxygen does not interfere the test compound due to purging the solution for at least 3 min with nitrogen gas to eliminate interfering oxygen.

The redox reaction of Cyclohexanone does not exhibit any significant peak because it can not delocalize electron in the structure. In the case of Benzophenone shows two reduction and one oxidation process which involving with one electron transfer in each step of reaction. The redox reaction is purely diffusion controlled and the first redox couple is chemical reversible ($I_{pa_1}/I_{pc_1} = 1$). The electrochemical behavior of Xanthone is so much similar to that of Benzophenone but the first redox couple is not completely chemical reversible ($I_{pa_1}/I_{pc_1} = 0.629$).

Cyclic voltammogram of α -Tetralone was similar to Anthrone which exhibits two redox couple in CH_3CN solution, both the first redox couple and second redox couple are purely diffusion controlled due to it exhibits a linear relationship between peak currents and square root of scan rate which follow Randles-Sevcik equation [$I_p = (2.69 \times 10^5)n^{3/2}AD^{1/2}v^{1/2}C^*$]. For the reaction of α -Tetralone can be summarized in Scheme 7. The first couple occurs at $E_1^{\circ'} = -1.749$ V vs NHE, the minimum reduction potential of all ketones. This suggests that the ketyl radical of α -Tetralone is quite unstable and can partially further react, which is different from Benzophenone. They probably due to the inability of the electron of ketyl radical to delocalize between two phenyl groups as in Benzophenone. The formation of ketyl radical of α -Tetralone occurs at more negative potential because of less possibility of resonance effect of

α -Tetralone hence less stability of the product than that of Benzophenone. This also increases the electron density at phenyl group and implements the different behavior from Benzophenone, i.e., the second oxidation to be able to occur. Due to the fact that there is only one carbonyl group, α -Tetralone inhibits the second reduction of the second carbonyl group as in quinones. Instead, the second reduction which occurs at very negative potential must be due to the phenyl group.

Anthrone behaves in a quite similar way to α -Tetralone, i.e., the first reduction couple (I, III) due to the formation of ketyl radical and the second reduction (II) due to phenyl group show in Fig 3. However, the first couple (I, III) occurs at much more positive potential (better reduction compared with Benzophenone), clearly reflecting the effect of the second phenyl group in addition to the presence of connecting carbon to facilitate electron delocalization in the radical product and hence increasing its stability. This also implements facile kinetics and chemical reversibility as can be seen from I_{pa_1}/I_{pc_1} is equal to 1.128 V and $\Delta E_{p_1} = 0.054$ V vs Ag/AgCl, very close to theoretical value, the distinctive behavior of Anthrone compared with α -Tetralone. By Randels-Sevcik relationship ($I_p = 2.69 \times 10^5 n^{3/2} AD^{1/2} CV^{1/2}$), this first process is diffusion controlled. The increase of the second reduction peak (II) is very high, compared with the first peak. This is due to the presence of one more phenyl group, is the proof that this peak corresponds to the reduction of phenyl group and suggests that the reduction can occur at both phenyl group and the total number of electron is multiple. Nevertheless, the product is unstable and the process of electron transfer is quite slow ($I_{pa_2}/I_{pc_2} = 1.796$ V, $\Delta E_{p_2} = 1.284$ V).

The electrochemical behavior of Xanthone is so much similar to that of Benzophenone. The first electrochemically and chemically quasi-reversible couple (I, III) is due to the reduction of carbonyl group. The fact that the second reduction peak (II) has somewhat less height, although there are two phenyl groups, without any corresponding (coupling) oxidation strongly indicates that this is due to the formation

of dianion by carbonyl group, not the phenyl one. The reaction scheme of Xanthone is therefore the same as that of Benzophenone. The reason that the second oxidation can not occur at the phenyl position, which is different from α -Tetralone and Anthrone, is probably that there is no connection (carbon with hydrogen only) between the phenyl group. This can make the delocalization of electron impossible. Ketones can be classified into two groups: those with two consecutive reductions both on the carbonyl group and on the carbonyl group followed by the phenyl group.

All quinones exhibit the same behavior, i.e., two redox couples. The first reduction reaction corresponds to the transformation of Q into semiquinone ($Q\cdot$) and the second to the transformation of $Q\cdot$ into quinone dianion (Q^{2-}). The presence of electron withdrawing group such as hydroxyl group helps stabilize the reduction product, hence the more positive reduction potentials as can be clearly seen in the case of Tetrahydroxybenzoquinone compared with Benzoquinone or dihydroxy derivatives compared with the parent Anthraquinone compound.

The ΔE_{p_1} of all quinones is somewhat higher than the theoretical value (>59 mV), reflecting that the electron transfer is quite slow at this scan rate (100 mV). Slow electron transfer at the electrode causes the peak separation to increase of the first couple. On the other hand, Damnacanthal ($\Delta E_{p_1} < 59$ mV) exhibits the peak separation is lower than all quinones. The first couple exhibits chemically reversible ($I_{pa_1}/I_{pc_1} = 1$) for all quinones except in the case of Tetrahydroxybenzoquinone and Damnacanthal which are not completely chemical irreversible.

All quinones are diffusion control of the current which they exhibit a linear relationship between peak currents and square root of scan rate (not shown), except Tetrahydroxybenzoquinone and Damnacanthal.

The differences of the anodic and cathodic peak potentials (ΔE_{p_1}) increases with increase of the scan rate from (0.1 to 0.6 V/s) also indicated non Nernstian behaviour (>59 mV). The presence of the substituent group has substantial effect on

the reduction potential, the electron withdrawing one implements more positive reduction potentials; i.e. Tetrahydroxybenzoquinone, Benzoquinone and 1,8-Dihydroxyanthraquinone respectively.

UV-Visible of complex of ketones with silver ion exhibits the mole ratio is equal to one to one in CH_3CN . On the other hand complex of quinone with silver ion is two to one respectively. The formation of the complex between silver ion and interesting compounds due to interact at carbonyl group in the structure.

Cyclic voltammograms (CVs) were obtained at CME in 0.2 M nitric acid solution contain 1.0×10^{-3} M of silver ion. The CVs of CME at which the anodic peak current of silver ion is larger than of unmodified. Thus there is a substantial accumulation of silver ion when the electrode modified with ketones and quinones. It was found that the quinones with more positive first reduction potential shows better affinity to silver ion because they help stabilize the reduction product. Anthrone would exhibit the best affinity to silver ion due to the fact that the order of more positive reduction potential of the first couple: Anthrone > Xanthone > Benzophenone > α -Tetralone > Cyclohexanone.

Quinones with higher positive reduction potential exhibit strong affinity to silver ion. Among quinones under investigation, therefore, Tetrahydroxybenzenequinone, p-Benzoquinone and 1,8-Dihydroxyanthraquinone should be the best modifier to attract silver ion. However Tetrahydroxybenzoquinone is very soluble in nitric acid so it can not use to be modifier in the chemically modified carbon paste electrode. This suggests the general trend that the best modifier should accept electron very well to further transfer to metal ions. This would help the selection of modifier in chemically modified carbon paste electrode or in catalysis.