THE CHRONOPOTENTIOMETRIC OXIDATION OF OXALIC ACID AT A PLATINUM ELECTRODE

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The purpose of this project has been to show, through means of chronopotentiometry, the inhibiting effect of various substances on the oxidation of oxalic acid at a platinum electrode. These substances, which decrease the chronopotentiometric wave for oxalate oxidation, can be divided into three categories. The first group consists of those substances that inhibit oxidation by being adsorbed on the elctrode. In this group are included chloride, bromide and thiocyanate ion and amyl alcohol. The second group consists of metal ions, such as nickel, aluminum and ferric, that readily form complexes with oxalate. The third effect studied was that of pH.

For the most part, the work consisted of recording potential vs. time graphs for the oxidation of oxalate under various conditions. In all cases, the oxalate concentration was 0.01 M, and was prepared from solutions of 0.05 M $KHOx \cdot H_2O$ or 0.10 M Na_2Ox. Before recording the chronopotentiograms the solution was deaerated with dry nitrogen gas, stirred, and allowed to become quiet. A cylindrical platinum wire electrode was used during most of the early experiments, but was later discarded in favor of a platinum button electrode. The most fundamental equation of chronopotentiometry, the Sand equation, which states that, $it^{\frac{1}{2}} = \frac{\pi^{\frac{1}{2}} nFAD^{\frac{1}{2}}C}{2}$, depends on the assumption that all processes are governed by linear diffusion[1]. By using the button electrode a better approximation of linear diffusion is obtained than if the cylindrical wire electrode were used.

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[1] Lingane, J. J.; "Electroanalytical Chemistry", Interscience Publishers, New York, 1958, p. 620.

The Effect of Cl^-, Br^-, SCN^- and Amyl Alcohol

In the study of adsorbants, Cl^- and Br^- were chosen because they are known to be readily adsorbed on the electrode. In the case of bromide the adsorbant is oxidized prior to the oxalate, and in the case of chloride the adsorbant is oxidized just subsequent to the oxalate, so that the resultant chronopotentiograms exhibit a double wave that makes it difficult to obtain quantitative results on the effect of these ions. At concentrations of chloride and bromide that are small in comparison to the concentration of oxalate in solution, however, it is noticeable that the oxalate wave has been decreased.

At concentrations of thiocyanate of 0.01 M and greater the SCN^- oxidation also overshadows the oxalate wave. At concentrations of SCN^- of 10^{-3} and 10^{-4} M, however, the SCN^- does not cause interference with the oxalate, and it can readily be seen that the oxalate wave has been suppressed.

The most fruitful investigation of this effect was carried out with amyl alcohol. Like many other organic substances, amyl alcohol is strongly adsorbed by the platinum electrode. Amyl alcohol is also oxidized, but at a potential above oxalate. Therefore, concentrations of alcohol greater than 0.01 M can be put in solution without distorting the oxalate wave.

Variable Concentrations of Amyl Alcohol (1 F H_2SO_4 , 0.01 M $Ox^{=}$)

$[C_5H_{11}OH]$	$(it^{\frac{1}{2}})/(it^{\frac{1}{2}})_0$
10^{-4} F	0.956
10^{-3} F	0.891
10^{-2} F	0.714
0.03 F	0.753
0.06 F	0.485
0.10 F	0.489

($(it^{\frac{1}{2}})_0$ is the value of $it^{\frac{1}{2}}$ with no amyl alcohol in solution.)

This data strongly suggests that in order to be oxidized, the oxalic acid must first be adsorbed on the electrode.

The Effect of Ni^{++}

In addition to Ni^{++}, Fe^{+++} and Al^{+++} ions were found to decrease the oxalate wave by complexation. Nickel, however, was chosen because it complexes the least readily with oxalate and the ratio of complexed to uncomplexed oxalate is therefore easier to control. In all cases the platinum wire electrode was used, the oxalate concentration was 0.01 M, and the solution was made 1 F in H_2SO_4.

Two investigations were carried out with nickel oxalate. First, the behavior of $it^{\frac{1}{2}}$ vs. i for oxalate at various concentrations of nickel was studied. Second, the behavior of $it^{\frac{1}{2}}/(it^{\frac{1}{2}})_0$ vs. temperature was studied at a concentration of Ni^{++} of 1 F. $(it^{\frac{1}{2}})_0$ is the value of $it^{\frac{1}{2}}$ for oxalate in 1 F H_2SO_4 with no nickel present at a particular temperature.

$it^{\frac{1}{2}}$ vs. i

$C_{Ni^{++}}$	i(mic.-amps)	$it^{\frac{1}{2}}$(mic.-amp.-sec$^{\frac{1}{2}}$)	$(it^{\frac{1}{2}})/(it^{\frac{1}{2}})_0$
0.1 F	150-600	745-683	0.90 - 0.82
0.5 F	100-500	510-485	0.61 - 0.58
1 F	80-300	416-322	0.50 - 0.39
2 F	45-80	220-160	0.26 - 0.19

$(it^{\frac{1}{2}})/(it^{\frac{1}{2}})_0$ @ Various Temperature

Temp.	i(mic.-amps)	$(it^{\frac{1}{2}})/(it^{\frac{1}{2}})_0$
2° C	70-120	0.266-0.366
25° C	80-300	0.423-0.549
40° C	250-500	0.545-0.575
50° C	300-600	0.596-0.732
60° C	300-700	0.538-0.624

From the values of $it^{\frac{1}{2}}$ taken at different current densities, i, it can been seen that the size of the oxalate wave depends on the current density as well as the nickel concentration. The effect of the Ni^{++} concentration is obvious. With increasing concentrations of Ni^{++} less oxalate is present in its uncomplexed form and thus available for protonation, adsorption and oxidation. The fact that $it^{\frac{1}{2}}$ varies with current density illustrates the fact that the slow kinetic step in this process is; $NiOx \rightarrow Ni^{++} + Ox^{=}$.

In chronopotentiometry we expect the product $it^{\frac{1}{2}}$ to remain constant if the concentration, electrode area and temperature are held constant. This , howver, is not true when slow kinetic steps are involved. At small current densities, the transition time, t, is considerably larger than at larger current densities, and in that additional time more NiOx dissociates. This additional dissociation increases the transition time and therefore the product $it^{\frac{1}{2}}$ even more because the concentration of oxalate in the diffusuon zone has been increased over its initial value during the oxidation process. Theoretically, $it^{\frac{1}{2}}$ is constant only if all kinetic processes are perfectly instantaneous; so there is always some variation of $it^{\frac{1}{2}}$ with i. This is noticeable only if the reactions are comparatively slow, as is the case in the dissociation of nickel oxalate.

The plots of $(it^{\frac{1}{2}})/(it^{\frac{1}{2}})_0$ vs. temperature and vs. current density show that the dissociation of NiOx is increased with temperature. It also further illustrates the point that the slope of the $it^{\frac{1}{2}}$ vs. i plots is determined by the rate of dissociation of the complex. At higher temperatures the values of greater current density start to become independent of current. At larger currents the time is so short that very little additional oxalate is supplied by dissociation, and the values of $it^{\frac{1}{2}}$ at these temperatures correspond to equilibrium concentration of oxalate in solution.

The Effect of pH

When the effect of pH on oxalate oxidation was studied, several rather remarkable facts were disclosed. At pH's lower than 3 the size of the oxalate wave was constant, but at pH 3 the oxalate wave began to decrease until it disappeared around a pH of 6. This effect is also apparently independent of the type of buffering medium used. The data that best illustrates these observations is reported below. This data was obtained at a Pt-button electrode, using a pH meter to read the potential and an automatic clock to record the time. The potential V_t, the potential at which the transition time was measured, was recorded from earlier chronopotentiograms.

pH	Buffer	V_t	i(microamps)	$it^{\frac{1}{2}}$(microamp-sec$^{\frac{1}{2}}$)
0.00	1 F H_2SO_4	1.25 V.	252-1010	1114-1195
1.42	Sulfate	1.15 V.	246-1005	1038-1329
2.10	Phosphate	1.15 V.	247-805	1128-1145
2.97	Phosphate	1.10 V.	200-695	816-847
4.55	Acetate	0.975 V.	150-410	390-717
5.93	Phosphate	0.85 V.	30-98	109-128

Data of $it^{\frac{1}{2}}$ vs. i for oxalate showed that $it^{\frac{1}{2}}$ is not a function of current density at the higher pH's. This rules out the possibility that the slow conversion of HOx^- and $Ox^=$ to H_2Ox is responsible for the decrease in the oxalate wave at higher pH's. The solution of this dilemma can be explained by the occurrence of oxide on the electrode.

If a chronopotentiogram is taken of oxalic acid using an electrode that has been electrically preoxidized the oxalate wave disappears. This is because the oxide on the electrode prevents the oxalic acid from being adsorbed and thus keeps it from being oxidized. It is therefore plausible to expect that oxidation of the electrode accompanies the oxidation of oxalic acid and causes the oxalate wave to be decreased. Since the oxidation of the electrode is pH dependent ($Pt + 2H_2O \rightarrow PtO_2 + 4H^+$) it is expected that at higher pH's the electrode becomes oxidized at a potential low enough to cause interference with the oxidation of oxalic acid. This corresponds with the observation that at higher pH's the oxalate wave is markedly decreased.

1 F H_2SO_4, 0.01 M $Ox^=$, 620 microamps

Potential of Preoxidation	$it^{\frac{1}{2}}$(microamp-$sec^{\frac{1}{2}}$)	$(it^{\frac{1}{2}})/(it^{\frac{1}{2}})_o$
0.8 V.	1123	0.97
1.0 V.	1074	0.92
1.2 V.	970	0.84
1.4 V.	878	0.76
1.5 V.	733	0.63
1.6 V.	-	-
0 V.	1161	-

pH 3 Phosphate Buffer, 0.01 M $Ox^=$, 620 microamps

Potential of Preoxidation	$it^{\frac{1}{2}}$(microamp-$sec^{\frac{1}{2}}$)	$(it^{\frac{1}{2}})/(it^{\frac{1}{2}})_o$
0 V.	973	-
0.9 V.	886	0.91
1.0 V.	756	0.78
1.1 V.	713	0.73
1.2 V.	588	0.61
1.3 V.	514	0.53
1.4 V.	-	-

$(it^{\frac{1}{2}})_o$ is the value of $it^{\frac{1}{2}}$ at an unoxidized electrode under the conditions of the experiment.

The fact that the amount of oxide adsorbed on the eletrode is a function of pH is born out in the tables given above. The two solutions used were 1 F H_2SO_4 and a solution buffered to pH 3 with phosphate. The electrode was preoxidized to various potentials in these solutions (the solutions contained no oxalate) and was then placed in a similar solution containing 0.01 M oxalate. Anodic current was then applied, and the oxalate wave at a partially oxidized electrode was recorded. A constant current was used in both cases to provide a better basis for comparison.

By comparing $(it^{\frac{1}{2}})/(it^{\frac{1}{2}})_0$ at the same potentials of preoxidation for the two pH's it is seen that the electrode is oxidized to a considerably greater degree at the higher pH. The oxidation of oxalic acid is therefore accompanied by oxidation of the electrode, and this is a function of pH. The oxalate wave thus begins to decrease as the pH is increased until finally sufficient electrode oxidation precedes the oxalate oxidation to comletely obliterate the oxalate wave.