

VOLTAMMETRIC STUDIES OF THE REDUCTION OF DIACETYL ON GLASSY CARBON ELECTRODE IN AQUEOUS SOLUTION

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ABSTRACT

Voltammetric studies of the reduction of diacetyl have been carried out in the pH range 0-10 in buffered aqueous solutions. The effect of pH, concentration of diacetyl and sweep rate on the peak current and peak potential is studied using cyclic voltammetry. Only one wave is observed except in the narrow range of pH 7-8 where two waves are observed. In the case of the first wave, under strongly acidic and slightly alkaline conditions, the process occurring at potentials corresponding to the limiting current region is controlled by diffusion while it is mixed controlled both by the rate of dehydration reaction and diffusion at intermediate pH conditions. The second wave which appeared in the pH range 7-8, is found to be diffusion controlled at the limiting current region.

From the steady state voltammetric measurements, the Tafel slopes obtained potentials corresponding to the foot of the first wave are found to be dependent on pH and diacetyl concentration.

Key Words : Voltammetry, diacetyl, glassy carbon-electrode

INTRODUCTION

Electrochemical reduction of diacetyl has been reported by many workers [1 - 5]. Polarography is the technique so far used in the study of reduction of diacetyl. Many contradictory reports [1 - 5] have appeared in the early studies regarding the number of reduction waves, the nature of species involved in the wave formation, the number of electrons involved in the reduction, and the pH dependence of the limiting current of the waves. Most of the authors [4 - 6] have indicated that polarographic reduction of diacetyl gives two waves at $\text{pH} > 7$. In the case of first reduction wave, it has been proved [4, 6] that nonhydrated diacetyl molecules undergo two-electron reduction to give acetoin as reduction product. The pH dependence of the limiting current of the first reduction wave and its other characteristics are also reported [6].

In the present work, the reduction behaviour of diacetyl on glassy carbon electrode (GCE) is studied using steady state voltammetry and cyclic voltammetry techniques.

EXPERIMENTAL

Voltammetric and cyclic voltammetric measurements were made in an H-type cell in which the cathode and anode compartments were separated by a G 3 sintered glass frit. A 5 mm diameter glassy carbon (Tokai) inserted into a glass tube

was used as the cathode whose exposed bottom disc surface acted as the effective area. The anode material was a platinum sheet. Saturated calomel electrode (SCE) was used as the reference electrode which was united to the working electrode through a capillary.

Solutions were prepared from double distilled water. Buffered solutions from phosphoric acid, acetic acid, sodium sulphate and sodium hydroxide acted as supporting electrolytes and the same were analytical grade chemicals. 0.1 M phosphoric acid and 0.1 M acetic acid were neutralised with sodium hydroxide and adjusted to the required pH. The ionic strength of the solution was maintained at 0.5 M by the addition of sodium sulphate. Laboratory grade diacetyl was distilled over a water bath before use. Experiments were carried out at a constant temperature of $31 \pm 1^\circ\text{C}$.

A potentiostatic three-electrode system was used in the voltammetric measurements. Potentials were applied from a potential scan generator through a potentiostat and the current output was recorded using a fast response X - Y recorder.

The glassy carbon disc surface was polished stepwise up to 4/0 emery to a mirror finish, degreased with trichloroethylene, washed with double distilled water and then inserted into the cell containing the supporting electrolyte.

Both catholyte and anolyte were the same. Purified hydrogen gas was passed through the catholyte for twenty minutes to remove the dissolved oxygen and passed above the solution during the electrochemical measurements. Both steady state voltammetric measurements and cyclic voltammetric measurements were made under unstirred conditions. The electrode surface was electrochemically pretreated at -1.00 V vs SCE for a few minutes before recording the background current. Each electrochemical measurement was made after passing hydrogen gas through the electrolyte and on the electrode surface for 2-3 minutes.

RESULTS AND DISCUSSION

General behaviour

Diacetyl gives one or two reduction waves on GCE depending on the pH of the solution. The first wave is observed throughout the pH range 0-10 while the second wave is observed only in the pH range 7-8.

Cyclic voltammetric behaviour of first wave

Figure 1 shows the cyclic voltammograms obtained for the reduction of $1.726 \times 10^{-2}\text{ M}$ diacetyl on GCE in 0.1 M phosphate buffer at pH 6.8 under different sweep rates. Single, well-defined peak is observed in the cathodic scanning and no complementary anodic peak is observed on the reverse scan.

Effect of pH on the shape of the cyclic voltammograms and on the peak parameters is studied by recording the cyclic voltammograms at different pH conditions. Only one wave is observed except in the pH range 7-8. At acidic pH conditions, only polarographic type limiting waves are obtained, due to the merging of hydrogen evolution current along with the reduction of diacetyl. Peak shaped cyclic voltammograms are obtained around neutral alkaline pH conditions. Table I shows the pH effect on the limiting current (i_L)/peak current (i_p) of the first reduction wave. The i_L/i_p is found to decrease with pH up to pH 7.6 and above that it increases. But when the pH of the solution is ≥ 8 , the i_p decreased with time and darkening of the solution occurs. These observations are in accordance with the recent study on the polarographic behaviour of diacetyl [6] in aqueous buffered solutions and the reported reason for the above observations is the aldol condensation of diacetyl in alkaline medium.

Peak potential, E_p , half peak potential $E_{p/2}$ and $E_{1/2}$ of the first reduction wave shifts to more negative values with increasing pH and this indicates that the protonated diacetyl molecules may be involved in the charge transfer reactions.

Cyclic voltammograms are recorded for the reduction of diacetyl at different sweep rates from $10\text{ mV}\cdot\text{sec}^{-1}$ to $1000\text{ mV}\cdot\text{sec}^{-1}$ (Fig. 1). i_p/i_L is found to increase linearly with

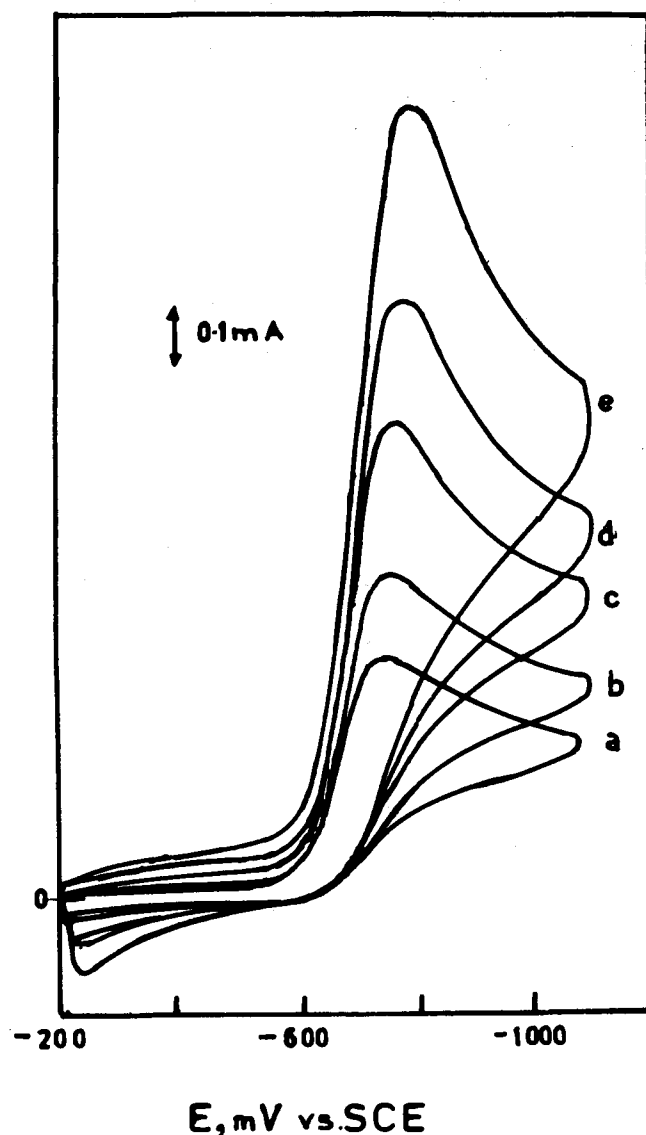


Fig. 1: Cyclic voltammograms for the reduction of $1.726 \times 10^{-2}\text{ M}$ diacetyl on GCE at pH 6.8 under different sweep rates a) $40\text{ mV}\cdot\text{sec}^{-1}$, b) $80\text{ mV}\cdot\text{sec}^{-1}$, c) $160\text{ mV}\cdot\text{sec}^{-1}$, d) $320\text{ mV}\cdot\text{sec}^{-1}$, e) $640\text{ mV}\cdot\text{sec}^{-1}$.

Table I: pH effect on the i_L/i_p for the reduction of diacetyl ($1.726 \times 10^{-2}\text{ M}$) on GCE

pH	Sweep rate $\text{mV}\cdot\text{sec}^{-1}$	i_L/i_p mA
0.8	100	1.08
2.0	100	0.65
4.0	100	0.64
6.0	100	0.63
6.8	100	0.60
7.6	100	0.550
8.4	100	0.660

sweep rate and current function values $i_p/V_{1/2}$, are found to be constant only at strongly acidic and alkaline pH conditions, as shown in Table II.

Table II: Effect of sweep rate on i_L/i_p , E_p and current function values ($i_p/V^{1/2}$) at different pH

pH	Sweep rate mV. sec. ⁻¹	i_L/i_p mA	E_p mV	$i_p/V^{1/2}$ $\times 10^{-3}$
0.8	20	0.52	—	3.6
	40	0.66	—	3.3
	80	0.87	—	3.0
	100	1.08	—	3.4
	160	1.23	—	3.7
	200	1.43	—	3.2
6.8	10	0.24	750	2.4
	20	0.31	755	2.19
	40	0.38	760	1.9
	80	0.52	762	1.83
	100	0.57	765	1.80
	160	0.71	770	1.78
	200	0.79	775	1.76
	320	0.94	780	1.66
	640	1.25	795	1.56
8.4	10	0.215	830	2.15
	20	0.30	840	2.12
	40	0.41	855	2.05
	80	0.56	865	2.00
	100	0.66	870	2.08
	200	0.93	885	2.07

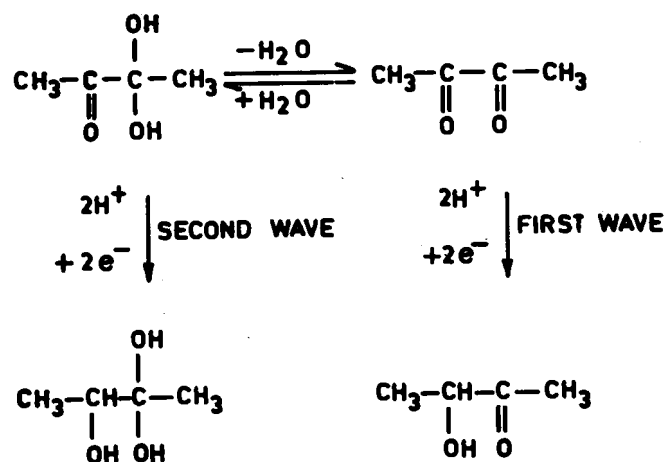
Similar observation is made for the variation of peak current with concentration of diacetyl. These experimental data have clearly indicated that at potentials corresponding to the limiting current region of the first wave, the process is controlled by diffusion at strongly acidic and slightly alkaline pH and is mixed controlled both by the rate of dehydration reaction and diffusion at intermediate pH conditions.

Peak potentials recorded at different sweep rates are found to shift in the cathodic direction with increasing sweep rate. This shift of E_p in the cathodic direction and the absence of anodic wave on the reverse can in the cyclic voltammetric studies have suggested that the process occurring at the limiting current and peak current regions is an irreversible one.

Polarographic studies of diacetyl [4] have shown that the first reduction wave discussed above is a two-electron

reduction of the non-hydrated form of diacetyl to yield acetoin.

Literature on diacetyl indicates that the compound is approximately 70 % hydrated, in one of the carbonyl groups in aqueous solutions at 25°C [7, 8]. Generally, monocarbonyl compounds which are hydrated [9-11] in aqueous solutions are not electroactive. These carbonyl compounds are electroactive when these are nonhydrated by acid and base catalysis. The recent polarographic studies of diacetyl reveal the fact that diacetyl being a dicarbonyl compound, both nonhydrated and monohydrated forms are electroactive but at different potentials.



Cyclic voltammetric behaviour of second wave:

The second reduction wave is observed in the present investigation only in a narrow pH range of 7 to 8. The cyclic voltammograms recorded at pH 7.6 for the reduction of diacetyl on GCE show two reduction waves as depicted in figure 2. The disappearance of the second wave at pH [12]. At the same time the value of the i_p of the first wave has increased. If the second carbonyl group of nonhydrated diacetyl molecules is involved in the second wave formation, the same is not expected to merge with the first wave at higher pH. Therefore, monohydrated diacetyl molecules are involved in the second wave formation. The disappearance of the second wave and increase of the first wave height at pH 8.4 and above, suggest that monohydrated diacetyl molecules are rapidly converted into non-hydrated form under such alkaline pH conditions.

The peak current values obtained for the two waves at pH 7.6 at various sweep rates and concentrations as shown in

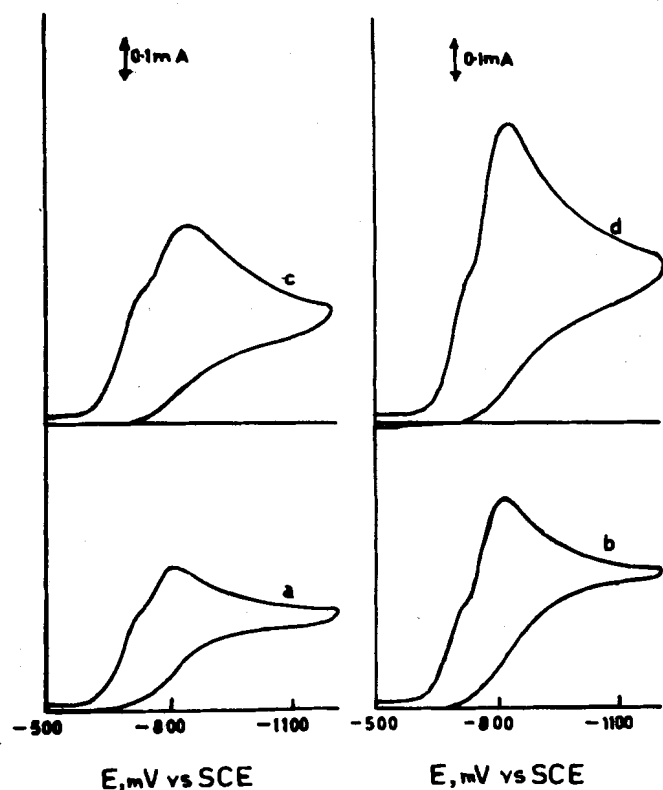


Fig. 2: Cyclic voltammograms for the reduction of diacetyl on GCE at pH 7.6

a) 1.726×10^{-2} M, $10 \text{ mV} \cdot \text{sec}^{-1}$, b) 2.877×10^{-2} M, $10 \text{ mV} \cdot \text{sec}^{-1}$,
c) 1.726×10^{-2} M, $20 \text{ mV} \cdot \text{sec}^{-1}$, d) 2.877×10^{-2} M, $20 \text{ mV} \cdot \text{sec}^{-1}$.

Table III: Peak current and current values obtained for the two waves at different sweep rates. pH 7.6

Diacetyl Conc. $\times 10^{-2}$ M	Sweep rate $\text{mV} \cdot \text{sec}^{-1}$	I wave		II wave	
		$i_L/(\text{mA})$	$i_p/(\text{mA})$	$i_p/V^{1/2}$ $\times 10^{-3}$	$i_p/V^{1/2}$ $\times 10^{-4}$
1.726	100	0.55	0.120	1.73	3.80
	160	0.68	0.240	1.70	6.00
	200	0.72	0.270	1.61	6.03
	320	0.82	0.340	1.45	6.01
	500	1.00	0.425	1.41	6.01
2.877	10	0.23	0.105	2.30	10.5
	20	0.31	0.160	2.19	11.3
	100	0.64	0.370	2.02	11.7
	200	0.90	0.490	2.01	10.9
4.604	10	0.25	0.25	2.50	25.0
	20	0.35	0.37	2.47	26.1
	100	0.66	0.68	2.08	21.5
	200	0.85	0.92	1.90	20.5

Table III, indicate the linear relationship between the i_p and sweep rates for both the waves. The current function values $i_p/V^{1/2}$ are also almost constant as shown in the Table III. These experimental data confirm that the processes occurring on the plateau of the two waves are controlled by diffusion.

Voltammetric behaviour of first wave

Steady state current potential curves for the reduction of diacetyl are recorded at different concentrations of diacetyl and different pH conditions. Tafel slopes which are obtained at potentials corresponding to the foot of the first wave, are found to be dependent on pH and concentration of diacetyl. The value of the Tafel slopes varies from 60 to 120 mV per decade change of current. Since the wave shifts with pH and concentration, reaction orders could not be found out. However, in strong acid and alkaline conditions where the limiting current is found to be primarily diffusion-controlled, Tafel slope is found to be 120 mV suggesting that at the foot of the first wave the first electron transfer is the rate-determining step in the overall process.

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