Studies on the Polarographic Behaviour of Benzil vis-a-vis the Kinetics of the Electrode Process

M.M.SRIVASTAVA, (Km) INDU BALA , MUKHTAR SINGH* & S.N.SRIVASTAVA+

Department of Chemistry, Agra College, Agra.

Polarographic behaviour of benzil (in 40% v/v, ethanolic solutions) has been studied as a function of pH using McI buffer. Two well defined waves are obtained in the entire pH range (2.2-7.6) investigated. While the first wave which corresponds to two-electron reduction process is irreversible and diffusion controlled, the second one is an adsorbtion wave. The kinetic parameters (αn_a & $k^{\circ}_{f,h}$) have been calculated by Koutecky's method. Besides, the influence of the concentration and nature of different supporting electrolytes and ionic and non-ionic surfactants on the kinetics of the irreversible electrode reaction of benzil has been investigated.

Studies on the polarographic reduction of aromatic diketones have been carried out by several workers [1-3]. Initial attempts were made by Pasternak[4] to study the polarographic reduction of benzil in various buffers and it was found that in each case a wave involving two electrons results. Stapelfeldt and Perone[5,6] studied the electrochemcial reduction of benzil in acid and alkaline media, and suggested a mechanism for its reduction. The studies on benzil undertaken so far relate to the determination of the variation of $E_{\frac{1}{2}}$ with pH with a view to arriving at the mechanism of its reduction at dme so far the electrode kinetics of its reduction of benzil at dme is concerned no work seems to have been done. The present study therefore aims at studying the polarographic reduction of benzil as a function of pH in McI buffer with special emphasis on the kinetics and mechanism of the electrode process at d.m.e. Besides, the effect of concentration and nature of different supporting electrolytes and ionic and non-ionic surfactants on the kinetics of the elctrode reaction of benzil has also been investigated.

EXPERIMENTAL

Benzil (Aldrich, Wisconsin, U.S.A.) was recrystallised from absolute alcohol before use. The other chemicals used were of BDH Analar grade. The concentration of depolarizer (in 40% v/v ethanolic solution) was maintained at 5.0×10^{-4} M. Desired concentrations of the various constituents of McI buffer viz., disodium hydrogen phosphate (0.5 M) and citric acid (0.25 M) were added to the solution to be polarographed. LiCl (0.1 M) was used as a supporting electrolyte. Requisite amount of Triton X - 100 (1.0×10^{-4}%) was added to supress the maxima. A manual polarograph (Toshniwal CLO_2 A) in conjuntion with a polyflex galvonaometer (PL 50) was used. All the measurements were made at 25 ± 0.1 ° C. The purified nitrogen was used for removing the dissolved oxygen. The potentials were measured against SCE.

The number of electrons (n) involved in the reduction of benzil at different pH was determined by millicoulometric method[7]. This gave the value of 'n' equal to 2 for the entire pH range (2.2- 7.6) investigated. Having known the value of 'n', Ilkovic equation was used to calculate the value of D, the diffusion-coefficient of benzil at different pH and also in the presence of increasing concentrations of the supporting electrolytes and surfactants. The potential-dependent rate constant, $k_{f,h}$ was calculated by Koutecky's method[8,9]. The kinetic parameters (αn_a & $k^{\circ}_{f,h}$) were calculated[10] from the plots of log $k_{f,h}$ Vs $E_{d.e}$. Throughout the measurements, the current at the end of the drop (i.e. the maximum current) was recorded for the reasons given by Meites[11]. The d m e. had the following characteristics :m =2.83 mg/sec; t= 3.15 sec; $m^{2/3} t^{1/6} = 1.614$ $mg^{2/3} sec^{-1/2}$, (in 0.1 M KCl, open circuit). h_{corr} = 50 cm.

RESULTS AND DISCUSSION

The depolarizer yields two well-defined waves in the entire pH range investigated. The two waves, however, do not appear to be of same nature. The second step appearing at more negative potentials is an adsorbtion wave[12], as evidenced by the characterstic plot of i_d vs $h^{1/2}_{corr}$. The first is diffusion controlled as the plot of i_d vs $h^{1/2}_{corr}$ is linear and passes through the origin.

Besides, the common tests[11] of irreversibility, a recent criterion based on cyclic voltammetry has also been applied. The ratio of I_{pa}/I_{pc} differs from unity and the value of separation in the peak potentials (280mV) clearly shows that

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* To whom correspondence may be made

+ Presently Vice-Chancellor, Kumaun University, Nainital, U.P.

the electrochemical reduction of benzil is irreversible.

The kinetic parameters ($\propto n_a$ and $k^\circ_{f,h}$) of the irreversible electrode reaction of benzil have been calculated and the values have been presented in Table 1.

TABLE 1

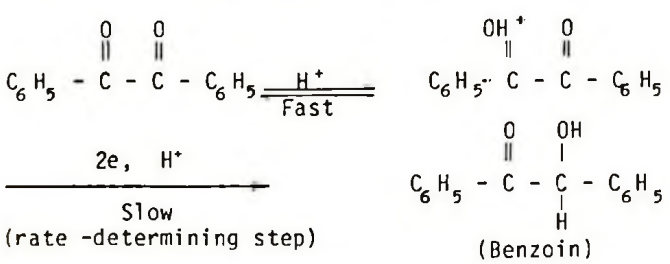
POLAROGRAPHIC CHARACTERISTICS AND KINETIC PARAMETERS FOR THE ELECTRODE REACTION OF BENZIL AT DIFFERENT pH VALUES OF McI BUFFER

pH	i_d μA	$-E_{\frac{1}{2}}$ volts	Slope (mV)	$Dx10^6$ (Cm^2 per sec)	$\propto n_a$	$k^\circ_{f,h}$ (Cm per sec)
2.2	3.48	0.33	72	7.38	0.74	$4.69x10^{-4}$
3.0	3.49	0.39	73	7.38	0.75	$3.56x10^{-6}$
4.0	3.36	0.47	73	6.88	0.74	$5.56x10^{-6}$
5.0	3.30	0.53	74	6.63	0.74	$1.84x10^{-7}$
6.0	3.24	0.55	73	6.40	0.74	$1.39x10^{-8}$
6.6	2.76	0.58	72	4.64	0.76	$2.26x10^{-9}$
7.0	2.76	0.65	71	4.64	0.75	$1.03x10^{-9}$
7.6	2.70	0.66	70	4.44	0.74	$3.08x10^{-10}$

The number of protons (p) involved in the rate-determining step of the reduction of benzil at dme has been calculated[13] from the slope of $E_{\frac{1}{2}}$ vs pH plots given by the equation.

$$\frac{dE_{\frac{1}{2}}}{d\,(pH)} = \frac{-\,0.05915}{\propto n_a} P \quad \ldots\ldots \text{(at 25°C)}$$

So far as the number of electrons involved in the rate determining step (n_a) is concerned, according to Meites[13] it is generally one. Having thus estabilished the stoichiometry of the rate-determining step for different ranges of pH, the following tentative mechanism can be proposed for the polarographic reduction of benzil:



Effect of concentration and nature of the supporting electrolytes on the kinetics of the electrode reaction of benzil :

The effect of concentration and nature of different supporting electrolytes viz., NaCl, NH_4Cl, KCl. LiCl, $MgCl_2$, NaBr and Na_2SO_4 on the kinetics of the electrode reaction of benzil has been studied at pH 4 of McI buffer. The kinetic parameters of the electrode reaction have been calculated at different concentrations (0.10 - 1.0 M) and the values have been listed in Table 2 which also includes the value of the potential-dependent rate constant $k_{f,h}$ at -0.46 V (SCE) which is nearly equal to $E_{\frac{1}{2}}$. Recently Singh and coworkers[14] have pointed out the inherent limitations of $k^\circ_{f,h}$ in interpreting the results with regard to the effect of certain experimental conditions on the kinetics of an irreversible electrode process, and have claimed that this can be studied from the variation in the value of $k_{f,h}$ at a selected potential which lies between the foot and the plateau of the wave. A perusal of Table 2 shows that the values of $\propto n_a$ & $k_{f,h}$ (at -0.46 V Vs SCE) decrease with the increasing concentrations of NaBr, NH_4Cl and Na_2SO_4. However, in the case of chlorides of Li, Na, K and Mg, there is an increase in the values. It indicates that the electrode reaction of benzil is rendered more irreversible with increasing concentrations of NaBr, NH_4Cl and Na_2SO_4 but becomes less irreversible with increasing concentrations of LiCl, NaCl, KCl and $MgCl_2$. This is supported by the fact that in the first case a negative shift in $E_{\frac{1}{2}}$ while in the latter a positive shift in $E_{\frac{1}{2}}$ takes place.

Effect of increasing concentrations of ionic and non-ionic surfactants on the kinetics of the electrode reaction of benzil :

The polarographic behaviour of benzil in presence of increasing concentrations of ionic and non-ionic surfactants has been studied at pH 4 of McI buffer. The following ionic and non-ionic surfactants have been used.

Cationic : Lauryl pyridinium chloride (LPC) and Cetyl pyridinium chloride (CPC) :

Anionic : Sodium lauryl sulphate (SLS) and Dodecyl benzene sulphonate (DBS): and

Non-ionic : Triton X-100 (polyethylene glycol ether of monoiso octyl phenol) and Gelatin.

In each case, wave-heights are diffusion-controlled and irreversible. The kinetic parameters of the electrode reaction have been calculated and the values are listed in Table 3. A perusal of Table 3 shows a decrease in the value of $\propto n_a$ which implies that the electrode reaction of benzil is rendered increasingly more irreversible with increasing concentrations of the surfactants. A decrease in i_d and a negative shift in $E_{\frac{1}{2}}$ (Table 3) with increasing

TABLE 2

POLAROGRAPHIC CHARACTERISTICS AND KINETICS PARAMETERS FOR THE ELECTRODE REACTION OF BENZIL IN THE PRESENCE OF INCREASING CONCENTRATIONS OF DIFFERENT SUPPORTING ELECTROLYTES AT pH 4. ALL POTENTIALS ARE w.r.t. SCE.

conc M	i_d (μA)	$-E_{\frac{1}{2}}$ (Volts)	Slope (mV)	D x 10^6 (cm²/sec)	αn_a	$k^*_{f,h} \times 10^6$ (cm/sec)	$k_{f,h} \times 10^4$ (cm/sec) -0.46 V
NaBr							
0.10	3.60	0.46	75	7.90	0.72	2.06	9.34
0.20	3.36	0.47	90	6.88	0.60	4.80	7.45
0.50	3.12	0.48	98	5.93	0.55	6.61	6.45
1.00	2.40	0.48	100	3.51	0.54	6.60	6.34
NH_4Cl							
0.10	4.09	0.47	100	10.14	0.54	8.15	9.62
0.20	3.84	0.48	105	8.99	0.52	7.95	6.85
0.50	3.50	0.49	118	7.90	0.46	0.88	5.88
1.00	3.60	0.51	122	7.90	0.45	0.93	4.30
KCl							
0.10	3.60	0.49	105	7.90	0.52	9.74	5.56
0.20	3.24	0.48	100	6.40	0.53	3.81	6.45
0.50	3.00	0.46	98	5.48	0.55	4.62	10.09
1.00	3.00	0.45	95	5.48	0.57	2.93	13.89
LiCl							
0.70	3.36	0.48	73	6.88	0.74	5.70	7.12
0.20	3.36	0.46	70	6.88	0.77	2.93	10.87
0.50	3.24	0.46	68	6.70	0.79	4.70	11.92
1.00	3.20	0.45	65	6.40	0.83	1.27	13.25
$MgCl_2$							
0.10	2.88	0.43	85	5.08	0.64	1.44	19.97
0.20	2.76	0.41	79	4.64	0.70	4.56	33.56
0.50	3.00	0.40	65	5.48	0.82	2.60	74.50
1.00	2.76	0.38	60	4.64	0.89	44.9	78.63
NaCl							
0.10	3.00	0.49	118	5.48	0.46	0.19	3.26
0.20	3.24	0.49	75	6.40	0.57	0.50	5.42
0.50	2.76	0.48	68	4.64	0.78	0.33	5.00
1.00	2.64	0.47	62	4.24	0.85	0.04	9.45
Na_2SO_4							
0.10	2.88	0.50	70	5.05	0.76	0.47	80.87
0.20	2.86	0.51	75	4.24	0.72	0.63	78.20
0.50	2.64	0.52	82	5.25	0.65	0.86	53.74
1.00	2.52	0.58	80	5.87	0.60	0.36	19.37

TABLE 3

POLAROGRAPHIC CHARACTERISTRICS AND KINETICS PARAMETERS FOR THE ELECTRODE REACTION OF BENZIL IN THE PRESENCE OF INCREASING CONCENTRATIONS OF IONIC AND NON-IONIC SURFACTANTS AT pH 4; ALL POTENTIALS ARE W.R. TO SCE.

Surfactant (M)	i_d (uA)	$-E_i$ Volts	Slope (mV)	$Dx10^6$ (cm^2 per sec	αn_a	$K^\circ_{f,h} x10^4$ (cm/sec) at-0.50V
Cationic - LPC						
* 5	3.36	0.48	90	6.88	0.60	15.75
10	3.18	0.50	100	6.16	0.54	11.37
100	3.00	0.53	110	5.48	0.49	4.82
500	2.88	0.56	142	5.05	0.39	2.72
Cationic - CPC						
* 5	3.36	0.47	80	6.68	0.67	24.24
10	3.24	0.50	120	6.40	0.46	10.28
100	3.12	0.51	130	5.93	0.41	8.72
500	3.12	0.56	135	5.93	0.40	4.04
Anionic - SLS						
* 5	3.36	0.48	100	6.88	0.54	15.79
10	3.30	0.51	105	6.63	0.52	8.66
100	3.24	0.24	112	6.40	0.48	3.40
500	3.24	0.57	120	6.40	0.45	2.66
Anionic - DBS						
* 5	3.30	0.50	100	6.64	0.55	10.48
10	3.24	0.52	120	6.40	0.45	5.99
100	3.24	0.54	125	6.40	0.43	5.31
500	3.18	0.59	128	6.17	0.42	2.66
Non-ionic -+Triton X-100						
* 100	3.36	0.47	73	6.88	0.74	21.00
500	3.12	0.51	100	5.93	0.54	6.51
1000	3.00	0.54	135	5.48	0.40	4.89
5000	2.76	0.58	142	4.64	0.38	2.12
Non-ionic -+Gelatin						
* 500	3.24	0.47	85	6.40	0.64	20.96
1000	3.00	0.49	100	5.48	0.50	11.58
5000	2.52	0.53	125	3.88	0.44	4.47

* Concentration at which the maximum gets just suppressed

\+ Concentration expressed in percentage

concentrations of surfactants lend support[15] to this conclusion. Potential-dependent rate constant ($k_{f,h}$) at -0.5 V (which is nearly equal to E_i) decreases with increasing concentrations of the surfactants thereby indicating that the electrode reaction of benzil is rendered more irreversible with increasing concentrations of the ionic and non-ionic surfactants. This observation is in harmony with the conclusion arrived at on the basis of the value of αn_a

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