

STUDIES ON THE POLAROGRAPHIC BEHAVIOUR OF NITROPHENOLS

Part II. *p*-Nitrophenol

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INTRODUCTION

THE polarographic behaviour of *o*- and *m*-nitrophenols described previously¹ indicates that their reduction is more or less similar in nature. *p*-Nitrophenol resembles the two isomers only at pH 2 and at other pH values larger number of waves are obtained. Unlike *m*-nitrophenol, the diffusion coefficient of *p*-nitrophenol shows a minimum at 50% ethanol resembling *o*-nitrophenol. In the present paper the polarographic behaviour of *p*-nitrophenol is described.

EXPERIMENTAL

The details of experimental procedure have been described previously.¹ Before the experiments the droptime is adjusted to 5 seconds a drop in 1 N potassium chloride. The capillaries used have the following 'm' values: 1.220, 1.227, 1.058 and 1.109 mg. per sec. The polarograms are taken at $30^\circ \pm 0.1^\circ$ C. *p*-Nitrophenol is prepared by nitrating phenol.² It is purified by recrystallization with aqueous ethanol, dried over phosphorus pentoxide in a vacuum desiccator. The para compound gives a maximum which can be suppressed by gelatin and hence 0.01% gelatin has been incorporated in the systems studied.

RESULTS

1. *Effect of Concentration of Ethanol on the Diffusion Current Constant, Half-wave Potential and $E_{\frac{1}{2}} - E_{\frac{3}{2}}$ Values at Various Acidities*

The results of analysis of the polarographic waves obtained under different conditions are given in Table I. As in the case of *o*- and *m*-nitrophenols two waves are noticed at pH 2. In neutral unbuffered solutions and solutions of pH 6 and 7, however, three waves are noticed. Even at pH 11,

TABLE I

Effect of concentration of ethanol on the polarographic behaviour of p-nitrophenol at different acidities

Conc. of p-nitrophenol: 0.5 mM. Conc. of lithium chloride: 1 M. Conc. of gelatin: 0.01% in aqueous ethanolic solutions.

pH	% ethanol by volume	E _{1/2} vs. S.C.E. (volt)			Diffusion current constant
		1st wave	2nd wave	3rd wave	
Neutral unbuffered solutions	0.0	-0.52	-0.87	-1.20	Total wave 11.53
	10.0	-0.54	-0.94	-1.16	10.41
	30.0	-0.64	-0.93	-1.19	7.93
	50.0	-0.79	-1.01	-1.20	7.02
	60.0	-0.82	-1.03	-1.20	7.38
	80.0	-0.85	-1.09	-1.25	7.09
	100.0	-0.89	Wave not quite visible		5.69
2	0.0	-0.27	Not measurable	Only two waves	1st wave 11.08 Total wave 11.91
	30.0	-0.33	-0.83		6.08 7.57
	50.0	-0.41	-0.81		5.34 6.29
	70.0	-0.43	-0.94		6.50 7.90
	100.0	-0.37	Only one wave appears		7.66 ..
6*	0.0	-0.47	-0.85	-1.13	Total wave 11.11
	30.0	-0.60	-0.95	-1.19	7.59
	50.0	-0.71	-1.03	-1.23	7.05
	70.0	-0.75	-1.07	-1.20	7.32
7*	0.0	-0.53	-0.85	-1.27	Total wave 11.33
	30.0	-0.68	-0.94	-1.23	7.65
	50.0	-0.77	-1.02	-1.24	6.71
	70.0	-0.81	-1.03	-1.18	6.56
11*	0.0	Only two waves appear	-0.88	-1.28	Total wave 11.05
	30.0		-0.97	-1.34	6.96
	50.0		-1.02	-1.31	6.68
	70.0		-1.06	-1.28	6.61

* Higher concentrations of ethanol produced precipitation.

where only one wave is noticed in the case of *o*- and *m*-isomers, two waves are obtained in the present case. Due to the complicated nature of the polarograms obtained, the half-wave potentials of the individual waves given in Table I are only approximate. Except at pH 2 where the diffusion current constants of the first and the total wave are given, only the diffusion current constant of the total wave is given in the table. The diffusion current constant shows a minimum at 50% ethanol in unbuffered solutions and solutions of pH 2 and 6. At pH 7 and 11, however, the diffusion current constant decreases and almost reaches a constant value at higher concentrations of ethanol. It is noteworthy that in neutral unbuffered solutions the diffusion current constant falls down to a low value in 100% ethanol. An increase in the concentration of ethanol at constant pH makes the half-wave potential more negative. At constant concentration of ethanol, increase in pH also makes the half-wave potential more negative indicating that the hydrogen ions are involved in reduction.⁹⁻¹¹ The $E_{\frac{1}{2}} - E_{\frac{1}{2}}$ values of all the three waves are found to be of the order 0.100 V indicating the irreversibility of the electrode process. In Table I, the results obtained with 0.5 mM *p*-nitrophenol are given. Experiments have also been carried out at various concentrations of *p*-nitrophenol and the results obtained are similar. The half-wave potential has been found to be almost independent of the concentration of nitrophenol and the diffusion current constant is constant within reasonable limits (Table III).

2. Relationship between the Diffusion Coefficient and the Diffusion Current Constant

In Table II, the diffusion coefficients of *p*-nitrophenol determined by the diaphragm cell method, viscosity method and equivalent conductivity method are given. The diffusion coefficients of the *m*-isomer as determined by the diaphragm cell method have also been included in the same table for comparison. It is noteworthy that the diffusion coefficient of *p*-nitrophenol shows a minimum at 50% ethanol. In this respect *p*-nitrophenol resembles *o*-nitrophenol¹ but differs from *m*-nitrophenol. The diffusion coefficients from the viscosity method decrease continuously with ethanol concentration without attaining any minimum value. As pointed out previously¹ the equivalent conductivity method gives only one value for the diffusion coefficient.

The diffusion current constant also shows a minimum at 50% ethanol in neutral unbuffered solutions and solutions of pH 2 and 6. However, in neutral unbuffered solutions the diffusion current constant decreases when the concentration of ethanol is increased beyond 70% reaching a low value

TABLE II

Diffusion coefficients and diffusion current constants of *p*-nitrophenol in aqueous ethanol solutions*

% ethanol by volume	Diffusion coefficient in sq. cm./sec. $\times 10^6$		Diffusion current constants of 0.5 mM. <i>p</i> -nitrophenol at various pH values†					
	Diaphragm cell method	Viscosity method	Neutral unbuffered soln.	2	6	7	11	
	<i>p</i> -isomer	<i>m</i> -isomer						
0.0	7.01	11.53	11.08	11.11	11.33	11.05
10.0	9.05	6.75	5.58	10.41
30.0	4.65	4.84	3.63	7.93	6.08	7.59	7.65	6.96
50.0	3.08	3.49	2.85	7.02	5.34	7.05	6.71	6.68
70.0	4.18	3.48	2.54	7.34	6.50	7.32	6.56	6.11
80.0	2.45	7.09
100.0	6.15	3.36	2.33	5.69	7.66

* Equivalent conductivity method gives a value of 9.68×10^{-8} sq. cm./sec. for the diffusion coefficient of *p*-nitrophenol.

† The diffusion current constant at pH 2 refers to the first wave only while in other cases it refers to the total wave.

in 100% ethanol. In solutions of pH 2, the diffusion current constant goes on increasing when ethanol concentration is increased beyond 50%, following closely the changes in the diffusion coefficient. At pH 7 and 11, the diffusion current constant reaches an almost constant value when the concentration of ethanol is increased beyond 50%. It is clear from previous investigations from this laboratory^{1, 3-5} that exact correspondence between the diffusion coefficient and the diffusion current constant ($I \propto D^{1/2}$) can be expected only when the value of 'n' is constant. It is rather interesting that in neutral unbuffered solution the diffusion current constant has decreased to a low value of 5.76 in 100% ethanol, although the diffusion coefficient has increased,

TABLE III

Effect of concentration of p-nitrophenol on the diffusion current constant in aqueous ethanol at various pH values

Conc. of lithium chloride: 1 M. Conc. of gelatin in aqueous ethanolic solutions: 0.01%.

pH	% ethanol by volume	Average diffusion current constant (total wave)	% deviation from the mean value	$m^{2/3}t^{1/6}$ in $\text{mg.}^{2/3} \text{sec.}^{-1}$
Neutral unbuffered solutions	0.0	11.30	2.0	1.417
	30.0	7.60	4.9	1.446
	50.0	7.02	1.0	1.473
	70.0	7.34 to 5.99	..	1.444
	100.0	5.73 (mean of 2 val.)	0.7	1.385
2	0.0	11.71	1.7	1.490
	30.0	7.35	3.9	1.358
	50.0	6.43 (Mean of 3 val.)	6.7	1.356
	70.0	7.90 to 7.03	..	1.461
	100.0 (1 wave only)	7.34	4.4	1.498
6	0.0	10.69	3.9	1.457
	30.0	7.24	4.8	1.351
	50.0	6.87	4.2	1.437
	70.0	7.32 to 6.22	..	1.471
7	0.0	11.12	1.9	1.376
	30.0	7.45	2.7	1.418
	50.0	6.66	2.1	1.445
	70.0	6.52	0.6	1.454
11	0.0	10.66	3.7	1.404
	30.0	6.97	2.6	1.291
	50.0	6.55	4.4	1.306
	70.0	6.23	1.9	1.446

3. *Effect of Concentration of p-nitrophenol on the Diffusion Current Constant at Various pH Values in Presence of Different Concentrations of Ethanol*

The results are presented in Table III. Only the average values of the diffusion current constants (five in ethanolic solutions and three in pure

aqueous solutions) are given. It is obvious that many of these base solutions can be used for the estimation of *p*-nitrophenol.

4. *Calculation of the Number of Electrons in the Reduction of p-Nitrophenol from the Ilkovic Equation*

The values of 'n' calculated employing diffusion coefficients from diaphragm cell only are given in Table IV, since the diffusion coefficients from viscosity and conductivity methods are not helpful in arriving at the reduction mechanism.

TABLE IV
'n' calculated from Ilkovic equation
Concentration of *p*-nitrophenol: 0.5 mM.

% ethanol	'n' at various pH values (Total wave)					
	Neutral unbuffered solution	2		6	7	11
		1st wave	Total wave			
10	5.7
30	6.1	4.6	5.8	5.8	5.8	5.3
50	6.6	5.0	5.9	6.6	6.3	6.3
70	5.9	5.2	6.4	5.9	5.3	4.9
100	3.8

DISCUSSION

1. *Variation of Diffusion Coefficient with Ethanol Concentration*

It has already been pointed out that *p*-nitrophenol resembles *o*-nitrophenol¹ in the minimum value for the diffusion coefficient at 50% ethanol. The value of 'D_η' (Table V) also shows a minimum in the present case. The apparent molar volumes of *p*-nitrophenol estimated by Stokes-Einstein equation using the diffusion coefficients by the diaphragm cell method are 22.11, 44.82, 74.84, 21.25 and 5.14 ml. at 10, 30, 50, 70 and 100% ethanol respectively as compared to a value of 94.73 ml. in pure solid state. It may therefore be concluded that viscosity factor alone does not account

for the variation of diffusion coefficient with ethanol concentration. As in the case of *o*-nitrophenol¹ the thermodynamic factor explains qualitatively the minimum in the value of the diffusion coefficient when different amounts of ethanol are incorporated in the base solution. It is possible that the variation in the diffusion coefficient is due to the combined effect of viscosity and thermodynamic factor.

TABLE V

Values of 'Dη' for p-nitrophenol at different concentrations of ethanol in neutral unbuffered solutions containing 1.0 M lithium chloride at 30° C.

% ethanol by volume	Diffusion coefficient by the diaphragm cell method $D \times 10^6 \text{ cm.}^2 \text{ sec.}^{-1}$	Viscosity poises $\times 10^3$ of the base solutions	$D\eta \times 10^8$
10.0	9.05	11.84	10.72
30.0	4.65	18.20	8.47
50.0	3.08	23.18	7.14
70.0	4.18	26.00	10.86
100.0	6.15	28.55	17.44

2. Mechanism of Reduction of *p*-Nitrophenol

Pearson⁶ has stated that in the case of *p*-nitrophenol the overall reduction process corresponds to the formation of amine at all pH values, two waves being obtained in all cases. The first wave corresponds to a four-electron reduction step in acid solutions while in alkaline solutions it represents a two-electron reduction process. Similar results have also been obtained by Page, Smith and Waller.⁷ These experiments, however, have been conducted employing low concentrations of ethanol and the reaction mechanism is given based on the value of '*n*' obtained by employing the diffusion coefficient obtained from equivalent conductivity method in the Ilkovic equation.

In neutral unbuffered solutions the total wave corresponds to reduction to amine when ethanol concentration is between 10 and 70%. But in 100% ethanol the value of '*n*' is 3.8 indicating the reduction to the hydroxylamine stage. At pH 2, 6 and 7 the total wave represents reduction to amine. The

first wave at pH 2 represents a mixed reduction process,¹ part of the molecules being reduced to hydroxylamine and part to the amine. At pH 11, however, the results indicate a six-electron reduction process at and below 50% ethanol. At 70% ethanol the value of 'n' falls to 4.9. The significance of this, however, is not clear. It may therefore be concluded that the presence of ethanol in the base solutions has a great influence on the course of reduction. Coulometric measurements, of course, will finally decide whether 'n' is really changing with ethanol concentration.

It has been noticed that in some base solutions, *p*-nitrophenol gives three waves. Similar observation has also been made in the case of *m*-nitrophenol though to a much lesser extent. It is rather difficult in such complicated cases to give the mechanism of reduction of the individual waves with any degree of certainty. Under these conditions it can only be concluded that reduction processes consisting of different number of electrons are occurring very near to each other due to closeness in the activation energy requirements.⁸

SUMMARY

The polarographic behaviour of *p*-nitrophenol has been studied in ethanol-water mixtures at different acidities. Three waves are noticed in neutral unbuffered solutions and solutions of pH 6 and 7. Two waves are observed at pH 11. These results are in contrast to those observed in the case of *o*- and *m*-nitrophenols. At pH 2, however, two waves are noticed as with *o*- and *m*-nitrophenols. The half-wave potential of all the waves becomes more negative both with an increase in pH and ethanol concentration. The values of $E_{\frac{1}{2}} - E_{\frac{2}{2}}$ indicate that the reduction process is irreversible in character. The proportionality between the diffusion current and the concentration of the reductant has been tested in various base solutions.

The diffusion coefficient of *p*-nitrophenol determined by the diaphragm cell method shows a minimum at 50% ethanol. This behaviour is similar to that noticed in the case of *o*-nitrophenol. The reduction mechanism of *p*-nitrophenol is discussed on the basis of 'n' calculated from the Ilkovic equation employing the diffusion coefficients obtained from the diaphragm cell method. Evidence is obtained for the formation of a mixture of different reduction products at the dropping mercury electrode. Difficulties in proposing reduction mechanism for individual waves has been pointed out.

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