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Electrochemical Reduction Behaviour of Some Substituted Epoxides

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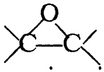
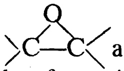
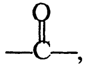
The electrochemical reduction behaviour of some substituted epoxides such as 1-(4-methyl)phenyl-3-phenyl-2,3-epoxypropan-1-one, 1-(4-amino) phenyl-3-phenyl 2,3-epoxypropan-1-one and 1-(2,4-dimethoxy)phenyl-3-phenyl-2,3-epoxypropan-1-one has been studied by employing advanced electrochemical techniques such as d.c. polarography, cyclic voltammetry and differential pulse polarography in the universal buffers of pH ranging from 2.0 to 12.0 in DMF-water mixtures. Millicoulometry is employed for the determination of number of electrons involved in the electrode process. Kinetic parameters such as diffusion coefficient and heterogeneous forward rate constant values are evaluated and reported. A reduction mechanism is proposed based on the results obtained. Differential pulse polarography is employed for the quantitative determination of all the three compounds in trace levels using standard addition and calibration methods.

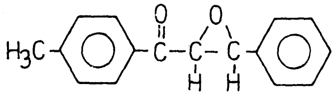
INTRODUCTION

Epoxy compounds are a group of cyclic ethers or allene oxides which have an oxygen atom attached to two adjacent carbon atoms. These compounds have found wide industrial use as chemical intermediates in the manufacture of solvents, plasticisers, cements, adhesives and synthetic resins[1,2]. The alpha epoxy compounds with the epoxy group  in the 1,2 position are the most reactive of the epoxy compounds and are primarily used in industrial applications. Epoxy compounds have the potential for adversely affecting the skin, mucous membranes, lungs, central nervous system and liver. The existence of the electroactive group of  and , which can be reduced at DME and HMDE allows the study of epoxides by voltammetry. Very little attention has been shown on the voltammetric behaviour of this important class of compounds. The aim of the present work is to carry out detailed studies on the reduction behaviour of some substituted epoxides

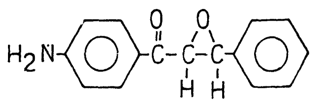
[1-(4-Methyl)phenyl-3-phenyl-2,3-epoxypropan-1-one] (I)

[1-(4-Amino)phenyl-3-phenyl-2,3-epoxypropan-1-one] (II)

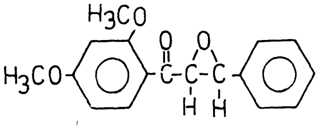
[1-(2,4-Dimethoxy)phenyl-3-phenyl-2,3-epoxypropan-1-one] (III)



I



II



III

in the solvent dimethyl formamide over a wide pH range from 2.0 to 12.0, to postulate the possible reaction mechanism for the electrochemical reduction of the compounds employing modern electrochemical techniques such as d.c. polarography, cyclic voltammetry and differential pulse polarography and to describe a procedure for the analytical determination of this compound in trace levels^4.

EXPERIMENTAL

Polarograms are taken with a polarographic analyser of model 364, Princeton Applied Research Corporation using BD8 Kipp and Zonen recorder. A three-electrode cell containing a dropping mercury electrode (flow rate 2.73 mg/s) is employed as the working electrode; a saturated calomel electrode (SCE) serves as the reference electrode. All diffferential pulse polarograms are recorded with E648 polarography combistand equipped with a mechanical drop timer. The electrochemical cell used has a provision for inserting the dropping mercury electrode, a reference electrode (Ag/AgCl(s), Cl^-) and a bubbler for deaerating the solutions and passing nitrogen over them when the polarograms are recorded so as to ensure an oxygen-free atmosphere. The dropping mercury electrode used had the following characteristics: area = 0.0223 cm^2 at the drop time = 2 sec, while the hanging mercury drop electrode (HMDE) had an area of 0.02323 cm^2 which was used to record cyclic voltammograms with metrohm unit E506 coupled with E612 VA scanner, E648 VA controller, E648 combistand and a digital electronics X–Y/t recorder. In all the above experiments platinum wire is used as the auxiliary electrode.

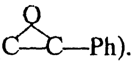
To prepare the epoxide, a mixture of appropriate chalcone, aqueous ethanol and H_2O_2 was taken in a two neck round bottom flask and it was kept under stirring using a mechanical stirrer. To this, an aqueous sodium hydroxide was added drop by drop and stirring was continued for 30 min. The product formed was distilled and washed thoroughly with cold aqueous ethanol. The purity of the compound was tested by melting point determination^3. Stock solution was prepared by dissolving the required amount of the compound in dimethylformamide (DMF). The universal buffers ranging from pH 2.0 to pH 12.0 were prepared using 0.2 M boric acid, 0.05 M citric acid and 0.1 M trisodium orthophosphate. All the chemicals used were of AnalaR grade and the solutions were prepared using triple distilled water. The test solutions were prepared by dissolving the required quantity of the stock solution and making up with the supporting electrolyte to the required volume to get the desired concentration and deaerated with oxygen-free nitrogen gas.

RESULTS AND DISCUSSION

The electrochemical reduction behaviour of the above I–III substituted epoxy compounds has been examined over the pH range of 2.0 to 12.0. In acidic and neutral solutions ($2 \geq pH \leq 6$), all the three compounds are found to be reduced in a single reduction process. The wave/peak corresponds to the $2e^-$ reduction of the epoxy group giving the corresponding hydroxy derivative. However, in alkaline solution ($pH \geq 8$) the reduction of the above three compounds are found to show a two step reduction wave/peak. It is assumed that the identical two electron reduction of epoxy substituent is followed by a mechanism corresponding to the two electron reduction of the keto group to the hydroxy derivative in all the three compounds. The representative voltammograms are shown in Figs. 1 and 2.

The epoxy group reduction is found to be diffusion controlled in the supporting electrolyte used as shown by the i_d vs. $h^{1/2}$ and $i_p/C_v^{1/2}$ vs. V relationships. The irreversibility of the electrode process is verified by logarithmic analysis of the wave. The slope of the E vs. log (i/i_{d-i}) graph exceeds appreciably 59/n mV and the numerical value[5] of $E_{1/4} - E_{3/4}$ exceeds 54.6/n mV. This observation along with the absence of anodic peak on the reverse scan in C.V. confirmed the reduction process to be irreversible.

The electrochemical data obtained for the different compound studied are presented in Tables 1–3. The $E_{1/2}$ and E_p values of the three compounds are found to be pH dependent and shift towards negative values with increase in pH of the buffer systems indicates the proton involvement in the electrode process. The proton involved in the rate determining step from $E_{1/2}$ vs. pH plots is found to be one.

In all the three compounds I–III the reduction potentials of epoxy group are found to be unaffected and almost equal because of the presence of phenyl group adjacent to the epoxy group (). However the keto group reduction potentials are influenced by the different substituents present in the benzene ring adjacent to the $-\overset{\overset{O}{\|}}{C}-$ group. Compounds II and III contain the amino ($-\ddot{N}H_2$) and dimethoxy ($-\ddot{O}CH_3$) groups respectively which contain lone pair of electrons. The reduction potential due to the keto group of compound III is found to be more negative than that observed for compound II. The dimethoxy groups which are in conjugation with the $-\overset{\overset{O}{\|}}{C}-$ group will facilitate more electron charge on the keto group than the $-\ddot{N}H_2$ group present in compound II, causing the reduction

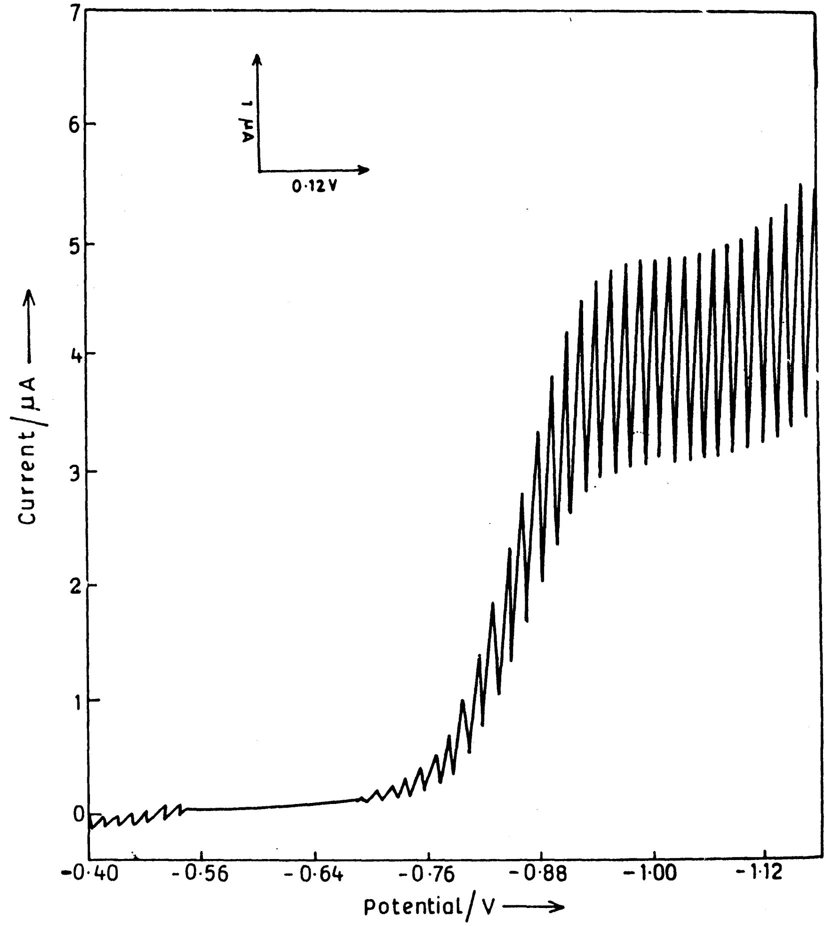


Fig. 1 Typical d.c. polarogram of 1-(4-methyl)phenyl-2,3-epoxy-propan-1-one in pH: 2.0 (concentration 0.5 mM, solvent 25% DMF, drop time 3 sec)

process to be difficult in compound III when compared to compound II. But the presence of the methyl group ($-CH_3$) in compound I has not shown any effect on the reduction of keto group because it does not contain a lone pair of electrons. Hence, the keto group in compound I is easily reduced when compared to that observed for compounds II and III. From the comparison of half-wave potentials of the above three compounds the ease of keto group reduction is observed to follow the order: Compound I ($-CH_3$) > Compound II ($-\ddot{N}H_2$) > Compound III (2,4-$\ddot{O}CH_3$).

Millicoulometric technique has been employed for the determination of number of electrons involved in the electrode process 'n' which is found to be two for both keto and epoxy group reductions[4] in pH 8.4. Product of the controlled

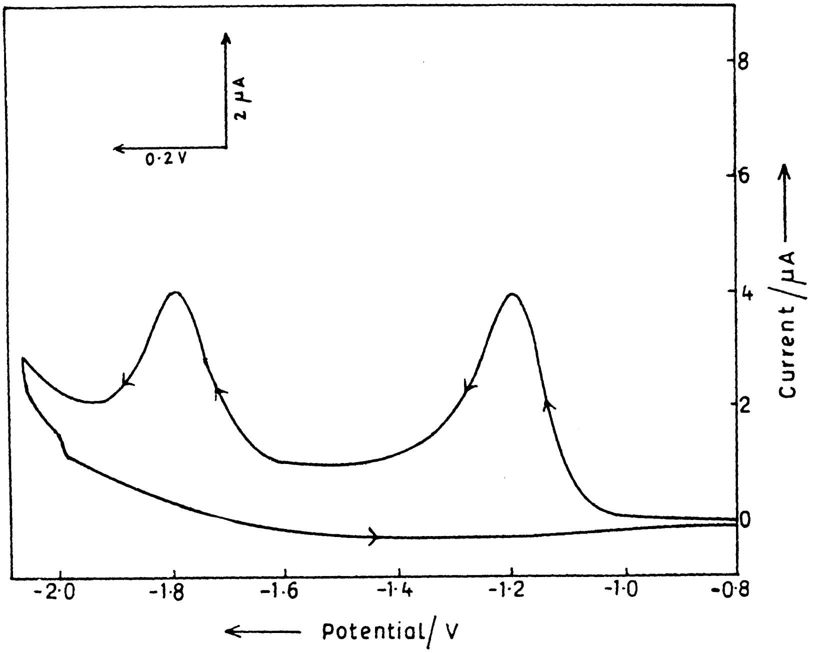


Fig. 2 Typical cyclic voltammogram of 1-(4-amino)phenyl-2,3-epoxypropan-1-one in pH: 12.0 (concentration 0.5 mM, solvent 25% DMF, scan rate 40 mVs^{-1}).

potential electrolysis of epoxides indicates the conversion of the keto and epoxy groups to hydroxyl groups.

The variation of diffusion current and peak current with the pH of the supporting electrolyte influences the diffusion coefficient values also to vary in the same manner. The reason for slight decrease in diffusion coefficient values with increase in pH may be attributed to the non-availability of protons with increase in pH[6,7].

The forward rate constant values are found to decrease with increase in pH as expected. This trend shows that the electrode reaction tends to become more irreversible with increasing pH of the solution[8]. The $k^{\circ}_{f,h}$ values for the reduction of epoxy group in I–III are found to be high when compared to that of keto group.

Based on the results obtained the following reduction mechanism can be proposed for the above three compounds under investigation.

Reduction Mechanism

In acid medium: $2.0 \geq pH \leq 6.0$

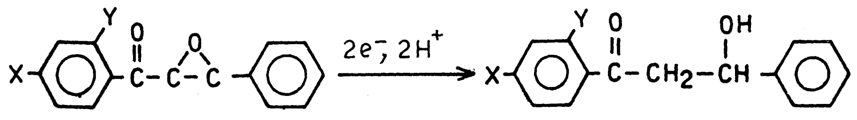


TABLE 1
TYPICAL ELECTRODE KINETIC DATA FOR 1-(4-METHYL) PHENYL-3-PHENYL-2,3-EPOXYPROPAN-1-ONE
Concentration = 0.5 mM Solvent = 25% DMF

pH of the supporting electrolyte		D.C. polarography (Drop time: 3 sec)			Cyclic voltammetry (Sweep rate: 40 mV s^{-1})			Differential pulse polarography (Drop time: 2 sec)		
		$-\frac{E_{1/2}}{V}$	$\frac{D \times 10^6}{(cm^2 s^{-1})}$	$\frac{k^{\circ}_{f,h}}{(cm\ s^{-1})}$	$\frac{-E_p}{V}$	$\frac{D \times 10^6}{(cm^2 s^{-1})}$	$\frac{k^{\circ}_{f,h}}{(cm\ s^{-1})}$	$\frac{-E_m}{V}$	$\frac{D \times 10^6}{(cm^2 s^{-1})}$	$\frac{k^{\circ}_{f,h}}{(cm\ s^{-1})}$
2.0		0.86	6.43	2.17×10^{-6}	0.85	6.25	3.33×10^{-7}	0.82	6.45	8.83×10^{-6}
4.0		0.92	6.32	5.43×10^{-8}	0.90	6.20	2.89×10^{-8}	0.90	6.30	2.91×10^{-7}
6.0		1.03	6.09	1.49×10^{-9}	1.01	6.12	1.03×10^{-10}	1.03	6.10	3.52×10^{-9}
8.0	(a)	1.09	5.85	3.44×10^{-10}	1.10	5.95	7.66×10^{-11}	1.08	6.01	1.92×10^{-11}
	(b)	1.61	5.72	8.12×10^{-18}	1.62	5.65	4.81×10^{-17}	1.60	5.25	3.33×10^{-19}
10.0	(a)	1.13	5.73	7.11×10^{-12}	1.15	5.83	4.90×10^{-13}	1.14	5.85	7.67×10^{-12}
	(b)	1.70	5.63	4.13×10^{-20}	1.69	5.60	9.12×10^{-19}	1.72	5.18	5.32×10^{-20}
12.0	(a)	1.19	5.65	4.15×10^{-14}	1.18	5.67	5.65×10^{-15}	1.19	5.61	5.01×10^{-14}
	(b)	1.78	5.25	5.59×10^{-21}	1.77	5.32	6.17×10^{-20}	1.78	5.05	2.72×10^{-21}

(a) First wave/peak (b) Second wave/peak

TABLE 2
TYPICAL ELECTRODE KINETIC DATA FOR 1-(4-AMINO)PHENYL-3-PHENYL-2,3-EPOXYPROPAN-1-ONE
Concentration = 0.5 mM Solvent = 25% DMF

pH of the supporting electrolyte		D.C. polarography (Drop time: 3 sec)			Cyclic voltammetry (Sweep rate: 40 mV s^{-1})			Differential pulse polarography (Drop time: 2 sec)		
		$-\frac{E_{1/2}}{V}$	$\frac{D \times 10^6}{(cm^2 s^{-1})}$	$\frac{k^\circ_{f,h}}{(cm\ s^{-1})}$	$\frac{-E_p}{V}$	$\frac{D \times 10^6}{(cm^2 s^{-1})}$	$\frac{k^\circ_{f,h}}{(cm\ s^{-1})}$	$\frac{-E_m}{V}$	$\frac{D \times 10^6}{(cm^2 s^{-1})}$	$\frac{k^\circ_{f,h}}{(cm\ s^{-1})}$
2.0		0.85	6.40	3.19×10^{-6}	0.86	6.28	9.43×10^{-6}	0.85	6.42	1.92×10^{-7}
4.0		0.92	6.32	4.72×10^{-8}	0.91	6.22	8.01×10^{-8}	0.90	6.28	4.49×10^{-8}
6.0		1.02	6.10	1.29×10^{-9}	1.03	6.13	1.92×10^{-9}	1.05	6.09	2.95×10^{-10}
8.0	(a)	1.09	5.82	4.08×10^{-11}	1.11	5.87	3.71×10^{-10}	1.09	6.00	6.54×10^{-11}
	(b)	1.64	5.70	8.21×10^{-19}	1.65	5.64	6.88×10^{-13}	1.63	5.32	1.25×10^{-20}
10.0	(a)	1.12	5.72	5.92×10^{-12}	1.16	5.80	7.71×10^{-13}	1.15	5.85	2.48×10^{-13}
	(b)	1.72	5.62	1.01×10^{-20}	1.72	5.59	2.19×10^{-20}	1.75	5.12	7.19×10^{-21}
12.0	(a)	1.20	5.64	1.45×10^{-14}	1.18	5.62	4.59×10^{-15}	1.20	5.62	8.01×10^{-14}
	(b)	1.80	5.24	9.19×10^{-22}	1.81	5.23	3.11×10^{-21}	1.80	5.18	2.22×10^{-22}

(a) First wave/peak (b) Second wave/peak

TABLE 3

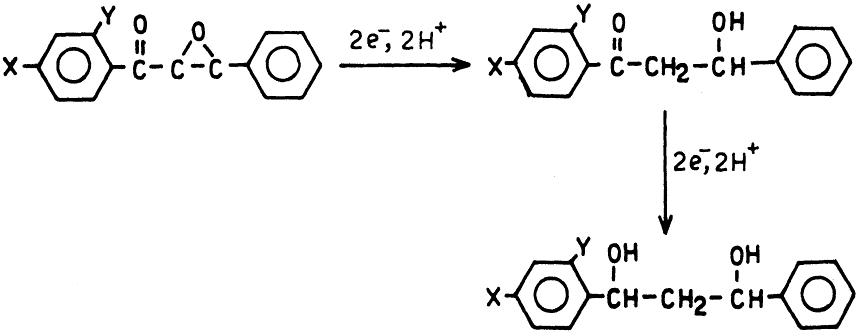
TYPICAL ELECTRODE KINETIC DATA FOR 1-(2,4-DIMETHOXY)PHENYL-3-PHENYL-2,3-EPOXYPROPAN-1-ONE

Concentration = 0.5 mM Solvent = 25% DMF

pH of the supporting electrolyte		D.C. polarography (Drop time: 3 sec)			Cyclic voltammetry (Sweep rate: 40 mV s^{-1})			Differential pulse polarography (Drop time: 2 sec)		
		$-\frac{E_{1/2}}{V}$	$\frac{D \times 10^6}{(cm^2 s^{-1})}$	$\frac{k^{\circ}_{f,h}}{(cm\ s^{-1})}$	$\frac{-E_p}{V}$	$\frac{D \times 10^6}{(cm^2 s^{-1})}$	$\frac{k^{\circ}_{f,h}}{(cm\ s^{-1})}$	$\frac{-E_m}{V}$	$\frac{D \times 10^6}{(cm^2 s^{-1})}$	$\frac{k^{\circ}_{f,h}}{(cm\ s^{-1})}$
2.0		0.87	5.45	3.12×10^{-6}	0.86	5.52	5.15×10^{-7}	0.84	5.42	2.17×10^{-6}
4.0		0.92	5.40	9.17×10^{-8}	0.91	5.42	2.92×10^{-8}	0.91	5.38	4.72×10^{-8}
6.0		1.02	5.32	2.12×10^{-10}	1.01	5.30	8.12×10^{-9}	1.03	5.17	1.44×10^{-10}
8.0	(a)	1.10	5.21	4.11×10^{-11}	1.12	5.15	3.17×10^{-11}	1.08	5.03	8.22×10^{-12}
	(b)	1.70	5.08	2.97×10^{-20}	1.69	5.02	4.99×10^{-19}	1.66	4.92	1.92×10^{-21}
10.0	(a)	1.14	5.05	8.81×10^{-12}	1.15	4.98	1.17×10^{-13}	1.14	4.92	5.55×10^{-13}
	(b)	1.79	4.87	5.55×10^{-22}	1.78	4.55	6.78×10^{-21}	1.80	4.85	2.14×10^{-23}
12.0	(a)	1.20	4.98	5.13×10^{-14}	1.19	4.85	2.99×10^{-14}	1.20	4.28	2.28×10^{-15}
	(b)	1.85	4.55	7.18×10^{-24}	1.86	4.33	3.17×10^{-24}	1.88	4.12	4.41×10^{-25}

(a) First wave/peak (b) Second wave/peak

In basic medium: $6.0 \geq pH \leq 12.0$



when X = $-CH_3$, Y = H Compound I
X = $-NH_2$, Y = H Compound II
X = $-OCH_3$, Y = $-OCH_3$ Compound III

Analysis

Differential pulse polarography is employed for describing analytical procedures for the estimation of epoxides using both calibration and standard addition methods. The optimum pH range for obtaining well resolved waves/peaks for the determination of epoxides is found to be $2 \geq pH \leq 6$. The peak current is found to vary linearly with the concentration of the electroactive species under investigation I, II and III over the range 1.0×10^{-5} M–2.15 10^{-7} M, 1.0×10^{-5} M–2.05×10^{-7} M and 1.0×10^{-5} M–2.12×10^{-7} M respectively. The best precision for standardisation is found to be obtained with drop time of 2 sec and a pulse amplitude of 50 mV. The standard deviation and correlation coefficient (for 10 replicants) are found to be 2.17%, 1.175%, 1.16% and 0.979, 0.981, 0.985 respectively.

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