# Defferential Polarographic Behaviour of Nitrogroup Containing Pesticides Dinitramine, Bromethalin and Isopropalin

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**Abstract**— In this work the effect of functional groups on the reduction potentials of nitrogroup containing pesticides such as dinitramine, bromethalin and isopropalin were studied.Differential pulse polarography, cyclic voltammetry, millicoulometry and controlled potential electrolysis were used for the determination of reduction potentials and electrode mechanisms.DME used as working electrode and universal buffer used as supporting electrolyte.

**Key words**— dinitramine, bromethalin and isopropalin, differential pulse polarography, DME, universal buffer.effect of pH, reduction potential.

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## 1 INTRODUCTION

NITRO group containing pesticides are playing vital role in the agriculture field. These pesticides are widely used as pre and post emergent weed control agents (herbicides) for a wide variety of crops, namely corn, sorghum, wheat, rice, sugar cane and for fruits, vegetables and wine yards, consequently, they are found in river water, [1-5 ]ground water [6,7] and soils.[8-10 ]Dinitro compounds were reported to exhibit significant antiproliferative and antiinfective activities against protozoan parasites includingLeishmaniaspp[11,12]Trypanosome broucei[13] and the intraerythrocytic forms of Plasmodium falciparum.[14 ]The electrochemistry of nitro group containing pesticides probably the one that has received much attention in recent years due tothe discovery that these compounds are present to varying degrees nearly in every section of the environment.[15] Though nitro group containing pesticides reduces easily under certain conditions the electrochemistry of nitro group is complicated due to dimerisation, coupling, tautomerisation and varios interferences that are formed during electrochemical process. Hence, the electrochemical mechanisms and analytical investigations of nitro group compounds are very impartent.

Shikata and co-workers [16, 17] have described the reduction of nitro group at DME in aqueous solutions. The behaviour of aromatic nitro compounds is some what defferent in aqueous systems [18]. In natural and alkaline solutions only the four proces occur with substituted hydroxylamine as the final product. In acidic solutions, both reactions occur with total 8 electrons per molecule transferred.

Pulse polarographic methods have been developed by Barker and Gardner [19] and latter was developed by Bond[20] and Keller[21]. In differential pulse polarographic technique, the current flowing at the working electrode sampled twice during the life time of each drop. The polarogram is plot of the current differences versus the base potential which varies in known fashion.

DPP has proved to be an excellent electroanlytical technique for the quantitative determination of organic compounds such as pesticides in trace levels. Smyth and Osteryoung [22] have studied the pulse polarographic behaviour of several pesticides. Arranz Valetin et al.[23] have examined the DPP behaviour of metamitron in aqueous media. Escudey [24] has studied the DPP behaviour of some pesticides. Wolff and Nurnberg [25] have used for micro and trace analysis for aromatic nitro compounds. DPP has also been employed in the analysis of paraquat,[26,27] ethafluralin,[28] glyphosphate[29].Jayarama Reddy[ 30-41] have employed this technique for mechanistic and analytical aspects of pesticides, drugs and pharmaceuticals.

## 2 EXPERIMENTAL

### 2.1 Apparatus and Electrodes

Polarographic assays were performed using a model 364 polarographic analyzer supplied by Princeton applied research corporation,(Princeton,NJ USA) coupled with a kipp and zonen BD8x-t recorder. A dropping mercury electrode(DME) was used as working electrode and a saturated calomel electrode(SCE) as the reference electrode.differential pulse polarograms were recorded with a unit supplied by metrohm (herisau,Switzerland)coupled with E 506 polarocard and E 612 VA scanner, cyclic voltamograms obtained by a digital electronic model 2000x-y/t recorder (Mumbai,India) in conection with the above unit. The DME used had an area of 0.223cm$^2$ at adrop time of 2s. A hanging mercury drop electrode (HMDE) used had an area of 0.223cm$^2$ in cyclic voltammetry. in all the above experiments platinum wire was used as auxillery electrodeallthe experiments were performed at 25$^0$C. pH mesurements were carried out with elico digital pH meter(Hyderabad,India).The millicoulometric apparatus used

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was supplied by radelkis( Budapest,hungary)cotrolled potential eklectrolysis was carried out using a techno potentiostat(tech.ini electronics, luknow,India) in amidified cell with a mercury pool cathode saturarted colomel reference electrode.

### 2.2 Reagents and Solutions

Pure samples obtained from rallis india limited.the purity of sample was tested with tin layer chromatography and melting point determinations.astock solution of pesticides under investigation were prepared in dimethylformamide.universal buffer cotaining 0.2Mboric acid, 0.05M citric acid and 0.1M trisodium orthophosphate were used as supporting electrolytes.

## 3 POLAROGRAPHIC STUDIES

Aliquots of stock standerd solution were diluted with appropriate amount of supporting electrolyte to yield a 1.0x$10^{-5}$M solution and the solution was purged with oxygen free nitrogen gas for 10min, then cyclic voltammetry (CV) and DPP current- voltage curves were recorded at the mercury electrode. All tables and figures will be processed as images. You need to embed the images in the paper itself. Please don't send the images as separate files.

### 3.1 Results and discussion

In this work highly effective and selective nitro group containing pesticides such as

A. Dinitramine

B. Bromethalin

C. Isopropalin

are chosen to understand the electrode kinetics and reduction mechanism concerned from the results of cyclic voltammetry, differential pulse polarography, controlled potential electolysis and millicoulometry in the universal buffer solutions of pH ranging from 2.0-12.0. Analytical procedures are described for their monitoring in various environmental samples by employing DPP method.

From the experimental results obtained for the electrochemical reduction behaviour of the above said compounds, the total number of peaks observed is found to be one. All the three compounds studied at pH range 2.0 to 12.0 (both acidic and alkaline medium).

### 3.1 differential Pulse Polarographic Behaviour

For dinitramine, bromethalin and isopropalin a single well defined peak (Figurs1, 2, 3) obtained and it is attributed to the simultaneous reduction of nitro groups to the corresponding hydroxylamine groups with an up take of eight electrons. In cyclic voltammetry, a small anodic peak is observed in the reverse scan. It is quite likely that a nitroso compound are formed, whose movement at the electrode surface may be responsible for the anodic peak at higher pH values (pH>10.0) for these three compounds. The reduction of nitro group is found to be facile in the above said compounds, apparently due to the orientation of different substituents to the surrounding nitro group. Among the three compounds dinitramine in comparison to bromethalin and isopropalin reduced at less negative potentials. This may be due to the presence of trifluoromethyl group in dinitramine. In case of bromethalin though it is having trifluoromethyl group it redused at greater negative potentials because of steric hinderence of tribromo benzine. Due to presence of propyl groups which make hindrance for the reduction in isopropalin may result high negative reduction potentials than above two compounds. Only hydroxylamine is the end product in dinitramine, bromethalin and isopropalin.

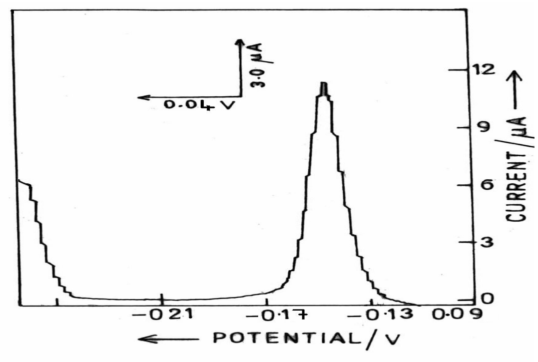


Fig 1: Differential pulse polarogram of dinitramine at pH: 4.0

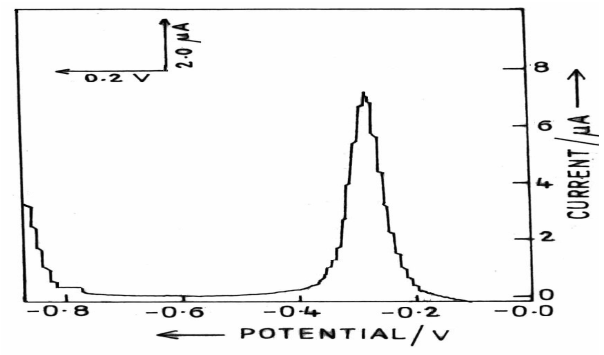


FIg.2: Differential pulse polarogram of bromethalin at pH: 4.0

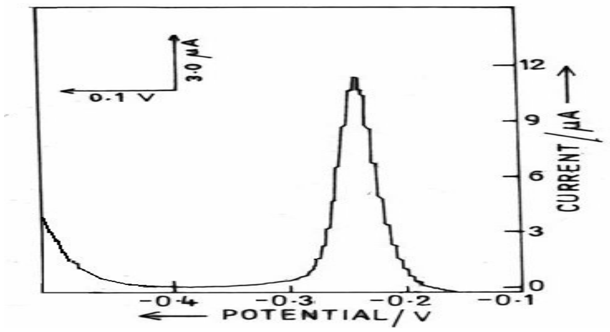


Fig.3: Differential pulse polarogram of isopropalin at pH: 4.0

### 3.1 Effect of pH

pH of the supporting electrolyte is found to influence the diffusion current and peak current values, which in turn changes the diffusion coefficient values in the same manner in all the compounds. The diffusion coefficient values obtained for the investigated compounds are found to be in good agreement in all the techniques. The heterogeneous forward rate constant values for the reduction of nitro groups in these compounds are observed to be high, since the nitro group reduction it facile which is evidenced from the less negative reduction potentials obtained. The rate constant values are seen to decrease gradually with increase in pH of the solution in all the techniques employed for these three compounds.

### 3.4 Characterisation of Waves/Peaks

Voltammetric behaviour of dinitramine, bromethalin and isopropalin has been studied over the pH range from 2.0 to 12.0. A single well resolved peak is observed throughout the pH range and this single peak is due to the simultaneous reduction of two nitro groups in eight electron process to the corresponding hydroxylamine groups. Typical cyclic voltammograms is shown in Fig 4,5,6. In cyclic voltammetric studies a small anodic peak, ($a_1$) is observed on the reverse scan at the higher pH values (pH > 10.0) for dinitramine. In the second scan, another small cathodic peak ($c_2$) at more positive potentials than $c_1$ is noticed. The anodic peak ($a_1$) may be due to the oxidation of hydroxylamine formed at ($c_1$) to nitroso derivative and the cathodic peak ($c_2$) may be attributed to the reduction of the nitroso derivative to the hydroxylamine again.

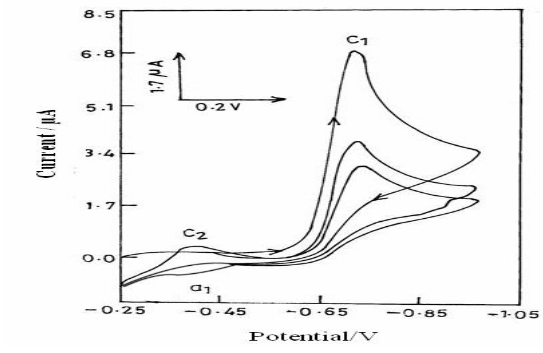
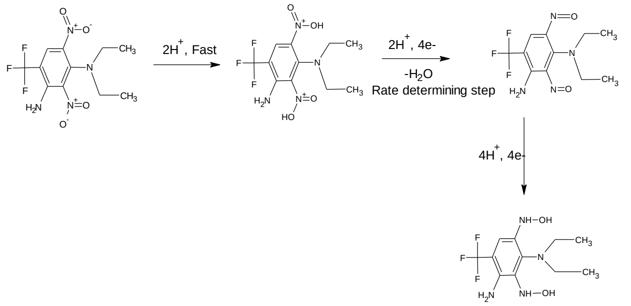
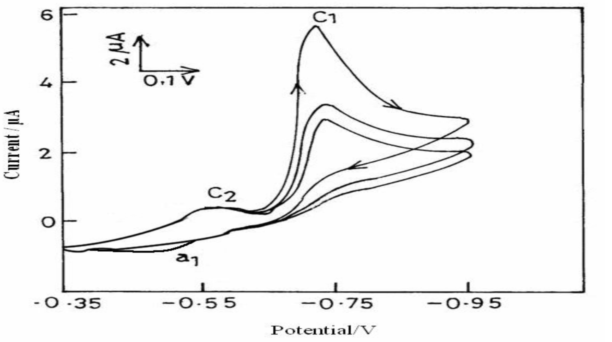


Fig. 4. Typical cyclic voltammogram of dinitramine at pH:4.0

## 4 REDUCTION MECHANISM OF NITROGROUP CONTAINING PESTICIDE



Scheme: 1. Reduction mechanism of dinitramine



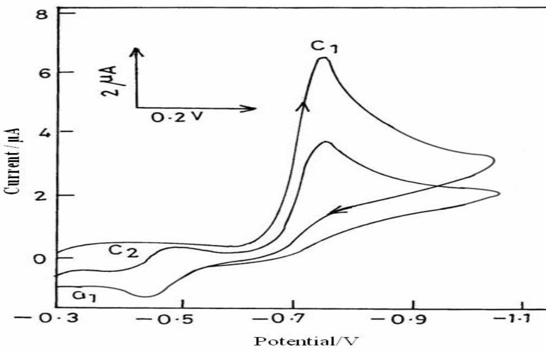
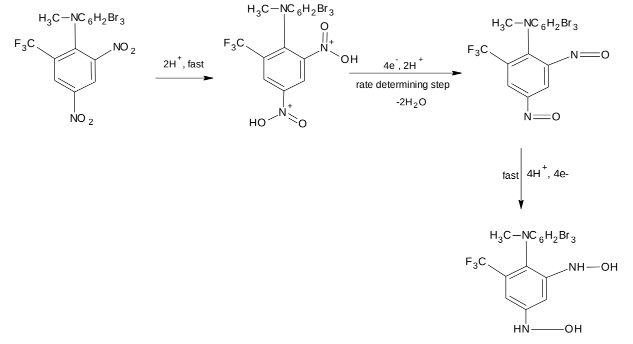


Fig. 6: Typical cyclic voltammogram of isopropalin at pH: 4.0.

The reduction mechanism of the dinitramine, bromethalin and isopropalin are shown in the scheme1, 2 and 3 respectively.



Scheme: 2. reduction mechanism of bromethalin

## 5 CONCLUSION

From this study it is concluded that electro analytical techniques are most suitable to determine molecular structure of a compound based on reduction potentials Based on this work it is concluded that electrochemical techniques are sensitive and less Expensive and less tidious compared to other techniques such as chromatography and, spectrophotometry.

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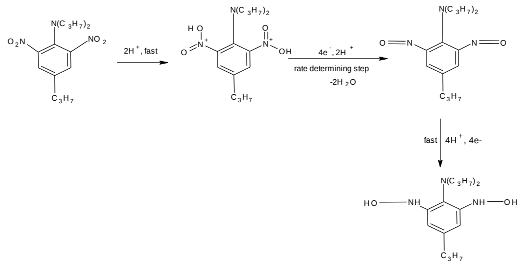

Scheme: 3. reduction mechanism of isopropalin