*Research Article*

# Electrochemical Study of Diphenyl Ether Derivatives Used as Herbicides

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The electrochemical behaviour of five nitro diphenyl ethers used as herbicides is investigated in acetonitrile. A detailed study by cyclic voltammetry and exhaustive electrolysis is carried out for the anodic oxidation of 2-Chloro-6-nitro-3-phenoxyaniline (*aclonifen*) and shows that the major oxidation product is a dimeric compound. A mechanistic scheme involving a coupling process is postulated for the electrochemical oxidation of this compound. Furthermore, the use of differential pulse voltammetry on a glassy carbon electrode permits the selective determination of *aclonifen*. The limit of detection is 0.6 $\mu$g/mL.

## 1. Introduction

The nitro diphenyl ethers (NDPEs) are commonly used as herbicides. The environmental contamination with these toxic molecules incited a number of studies concerning their occurrence and determination in various matrixes such as environmental waters and food by means of chromatography and related techniques [1–15]. The number of electrochemical studies concerning the NDPE derivatives are less numerous, even if the electrochemical approach is known to be effective both for analysis and destroying of various toxic compounds [16–20].

This paper reports the electrochemical behaviour of a series of p-nitro diphenyl ether derivatives: *aclonifen, bifenox, acifluorfen, nitrofen,* and 4-nitro diphenyl ether parent compound. Scheme 1 presents the chemical structures of the selected molecules which are considered as multi-target herbicides.

The corresponding chemical structures cumulate various functions presuming some electroactivity. Thus, the nitro aromatic functional group is reducible with a characteristic cathodic wave. This has been observed in protic and aprotic media for *bifenox* and *nitrofen* [21, 22]. The present investigation is focused on the anodic behaviour of the concerned

NDPE derivatives. This has not been described in the literature. A detailed study is performed in the case of *aclonifen* using cyclic voltammetry and exhaustive electrolysis. The results allow proposing a mechanistic scheme for its anodic oxidation. Furthermore, the anodic behaviour of *aclonifen* is analysed by means of differential pulse voltammetry (DPV), which is shown to be a sensitive method permitting a rapid determination of the concerned herbicides.

## 2. Experimental

*2.1. Electrochemical.* The electrochemical measurements are made in acetonitrile in the presence of tetrabutylammonium tetrafluoroborate (NBu$_4$BF$_4$) 0.1 M as the supporting electrolyte.

The voltammetric study is performed with a Voltalab 80 analyser from radiometer. The working electrode is a 3 mm diameter glassy carbon disk.

The exhaustive electrolyses are carried out at a constant potential located on the first wave. They are performed with a PTJ 35-2 potentiostat and an IG5 integrator both from Tacussel. The separated cell is equipped with a platinum grid (4 cm$^2$) and a platinum wire, respectively, as the working and
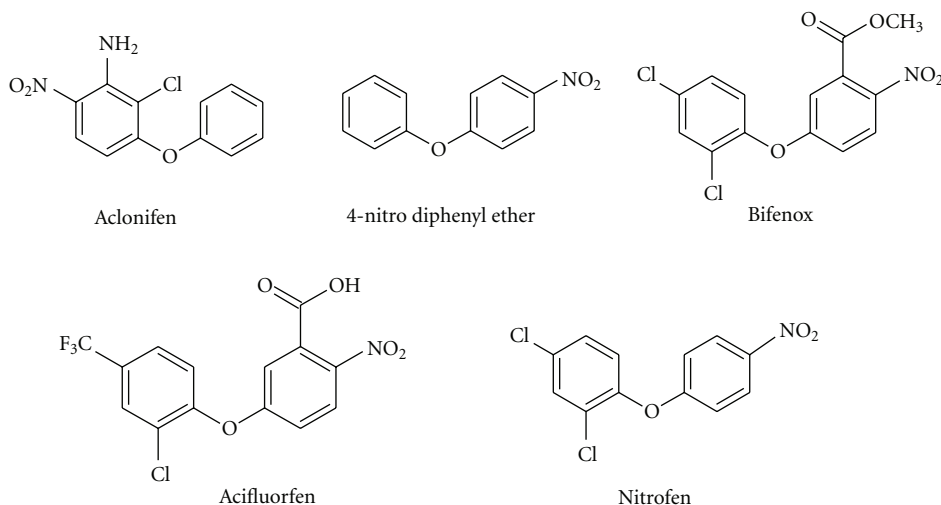
Scheme 1: Names and chemical structures of the studied nitro diphenyl ether derivatives.

the auxiliary electrode. The reference is a saturated calomel electrode (SCE). The electrolysis solutions are evaporated then extracted with chloroform before chromatographic analysis.

The differential pulse voltammetry is performed with a POL 150 radiometer analyser associated with MDE 150 stand equipped with a glassy carbon disk as the working electrode.

*2.2. HPLC/MS.* The electrolysis products are separated and analysed by HPLC with a C-18 column (150 mm × 4.6 mm and 5 $\mu$m particle size) at 40°C. The mobile phase is a mixture of water/acetonitrile (40/60). A DAD detector is used. The mass spectrometric analysis is performed with an Agilent 1100 MSD triple-quadrupole in the APCI negative mode. Nitrogen is the nebulizer and the collision gas. The analysis parameters are fixed as follows: $T$ = 400°C; gas flow: 12 L/min; nebulizer gas pressure: 50 psi; capillary voltage: 5000 V; corona current: 4 $\mu$A.

*2.3. Chemical.* The studied compounds: *aclonifen, bifenox, acifluorfen, nitrofen, 4-nitro diphenyl ether,* and the supporting electrolyte tetrabutylammonium tetrafluoroborate are from Fluka. The solvent acetonitrile (HPLC quality) is purchased from Panreac.

*Aclonifen Oxidation Product.* Characterisation of the main product of the electrochemical oxidation of aclonifen is achieved in the electrolysis solution using HPLC/mass spectrometry coupling, ultraviolet-visible absorption, and FTIR spectrophotometry.

(i) *Mass spectrum*: $m/z$ = 524 (100%), 526 (70%), 528 (10%); 390 (5%); 249 (3%). The molecular cluster is composed of peaks at $m/z$ = 524, 526 and 528. This result perfectly fits the empirical formula $C_{24}H_{14}Cl_2N_4O_6$ containing two chlorine atoms and leads to the isotopic distribution: $C_{24}H_{14}^{35}Cl_2N_4O_6$, $C_{24}H_{14}^{35}Cl^{37}ClN_4O_6$, and $C_{24}H_{14}^{37}Cl_2N_4O_6$.
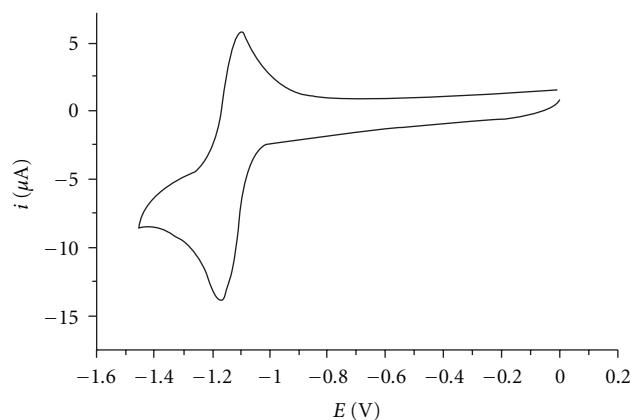


Figure 1: Reduction voltammogram of *aclonifen*. Acetonitrile, $NBu_4BF_4$ 0.1 M, $C$ = 0.5 mM, $v$ = 100 mV s$^{-1}$, glassy carbon disk ($d$ = 3 mm), reference: SCE.

(ii) *FTIR spectrum*: wave number (cm$^{-1}$): 2970–2930 (C–H); 1444 (N=N); 1405, 1376 (C–NO$_2$); 1200–1250 (C–N); 1039, 1060 (C–O); 751 (C–Cl).

(iii) *UV-visible spectrum*: $\lambda_{max}$ = 299 nm; 498 nm (>2300 mol$^{-1}$L cm$^{-1}$).

## 3. Results and Discussion

### 3.1. Voltammetric Study

*3.1.1. Cathodic Reduction.* The voltammetric study shows that all compounds except *acifluorfen* have similar cathodic behaviours. A single reversible peak is obtained as observed in Figure 1, illustrating the reduction voltammogram of *aclonifen*. This is attributed to the formation of a stable anion radical at the concerned time scale. The reduction peak characteristics are given in Table 1.
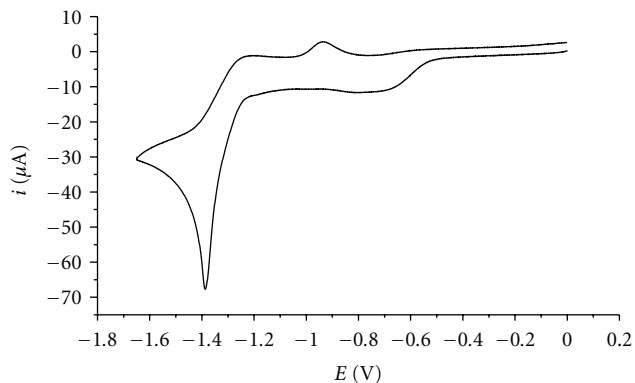
FIGURE 2: Reduction voltammogram of *acifluorfen*. Acetonitrile, $NBu_4BF_4$ 0.1 M, $C = 2$ mM, $v = 100$ mV s$^{-1}$, glassy carbon disk ($d = 3$ mm), reference: SCE.

TABLE 1: Reduction of nitro diphenyl ether derivatives. Acetonitrile, $NBu_4BF_4$ 0.1 M, $C = 1$ mM, $v = 100$ mV s$^{-1}$, glassy carbon disk ($d = 3$ mm), reference: SCE.

| Compounds | $E_{pc}$ (V) | $\Delta E_p$ (mV) |
|---|---|---|
| Aclonifen | −1.165 | 0.062 |
| Bifenox | −1.031 | 0.057 |
| nitrofen | −1.446 | 0.063 |
| 4 Nitro DPE | −1.606 | 0.061 |
| Acifluorfen | −1.384 | * |

$E_{pc}$: cathodic peak potential; $\Delta E_p$: width of the reversible. cathodic peak.
*irreversible peak.

It appears that the electrochemical reversibility is not affected by the substitution of the nitroaromatic ring by various groups such as Cl, $NH_2$, $CO_2H$, and $COOCH_3$, whereas in the same time, the reduction potential is noticeably modified.

A*cifluorfen* behaves in a different manner as shown in Figure 2. The cyclic voltammogram involves two cathodic peaks, both irreversible. The first one is a "plateau"-shaped monoelectronic wave. The second peak corresponds to the exchange of approximately 3 electrons. Thus, the presence of an acidic group neighbouring the nitro functional group induces very probably an intramolecular deactivation of the anion radical.

### 3.1.2. Anodic Oxidation.

The oxidation voltammograms of the studied compounds have a rather similar pattern. The obtained anodic peaks do not show any reversibility on the reverse scan. The corresponding data are given in Table 2. They show that the studied diphenyl ether derivatives are oxidized at potentials superior to 1650 mV/SCE. In addition, for all compounds, excepted *aclonifen*, the current peak is high and implies the exchange of an important number of electrons. The corresponding $n_e$ values are obtained by calculating the current ratio $i_{Pa}/i_{Pc}$, $i_{Pa}$, and $i_{Pc}$ are, respectively, the oxidation and reversible reduction peak currents. The obtained high values suggest that the anodic oxidation of diphenyl ether derivatives proceeds

TABLE 2: Oxidation of nitro diphenyl ether derivatives. Acetonitrile, $NBu_4BF_4$ 0.1 M, $C = 1$ mM, $v = 100$ mV s$^{-1}$, glassy carbon disk ($d = 3$ mm), reference: SCE.

| Compounds | $E_{pa}$ (V) | $n_e$ |
|---|---|---|
| Aclonifen | 1.714 | 2.2 |
| Nitrofen | 1.924 | 4.2 |
| Bifenox | 2.237 | 4.3 |
| 4 nitro DPE | 1.649 | 4.3 |
| Acifluorfen | 2.531 | 3.3 |

$E_{pa}$: anodic peak potential;
$n_e$: number of exchanged electrons

via a complex mechanism. Several electron transfers and associated chemical reactions are involved. In fact, further information is required for clarifying the anodic process. This concerns especially the oxidation products.

In the following, we report the more detailed investigation concerning the electrochemical oxidation of *aclonifen*. The study is performed at the voltammetric and exhaustive electrolysis scales.

As observed in Figure 3, the oxidation voltammogram of *aclonifen* exhibits two anodic peaks. The first one is well defined and the corresponding number of electrons exchanged per mole is close to 2.
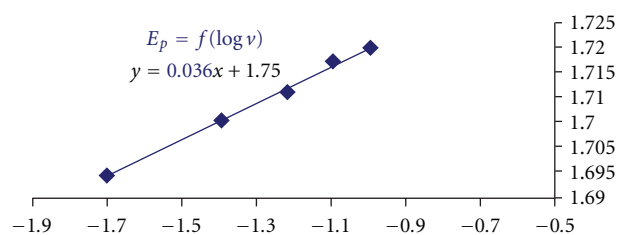
Furthermore, the peak potential variation as a function of the scan rate gives a linear $E_p = f(\log v)$ graph, the slope is approximately 30 mV (Figure 4). We notice that the concentration does not affect the $E_p$ value. These results are consistent with an ECE type mechanism, the chemical step being a first-order deactivation of the cation radical ensuing the first electron transfer.

### 3.2. Exhaustive Electrolysis.

The exhaustive electrolyses of *aclonifen* are carried out at a constant potential ($E = 1.7$ V/SCE) located at the first anodic peak. They are stopped after the consumption of 2 F/mole. The HPLC-mass spectrometric analysis of the electrolysis solution shows that the major oxidation product is a dimeric compound deriving from the starting material. The molecular weight is around 524. Furthermore, the mass spectrum given in the experimental section shows a molecular cluster at m/z: 524 (100%), 526 (70%), and 528 (13%) compatible with the presence of two chlorine atoms. The peak at m/z = 249 is probably due to the elimination of a nitrogen molecule from the molecular ion of the azo compound which derives from aclonifen (Scheme 2).

The proposed chemical structure is supported by the spectrometric analysis in UV-visible range. Actually, a significant absorption is observed at 498 nm, which may be attributed favourably to a nitrogen double bond of a substituted azobenzene. Moreover, when comparing the FTIR spectrum of the electrolysis solution to that of aclonifen, there is a new band located at 1444 cm$^{-1}$ which can be attributed to the N=N. These results suggest that dimerization is the predominant pathway in the anodic oxidation of aclonifen. It is worth noticing that this type of oxidative coupling has been described in the literature for
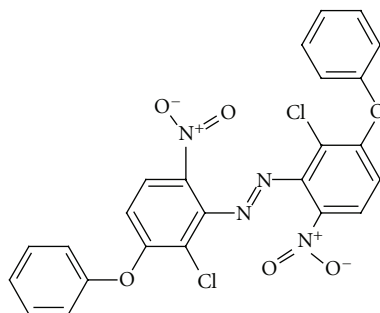
SCHEME 2: chemical structure of the major oxidation product of *aclonifen*.
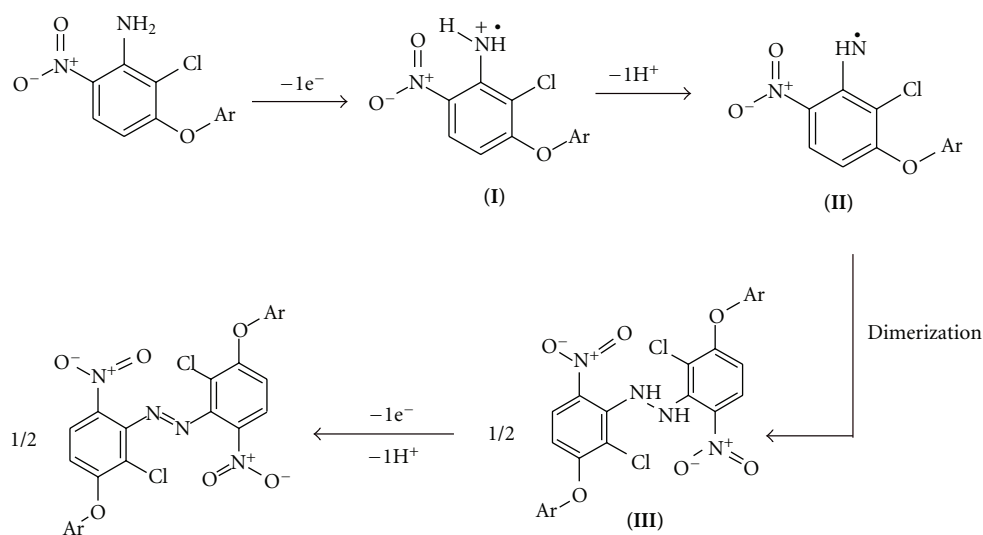


SCHEME 3: Mechanism of the anodic oxidation of aclonifen Ar : $C_6H_5$.
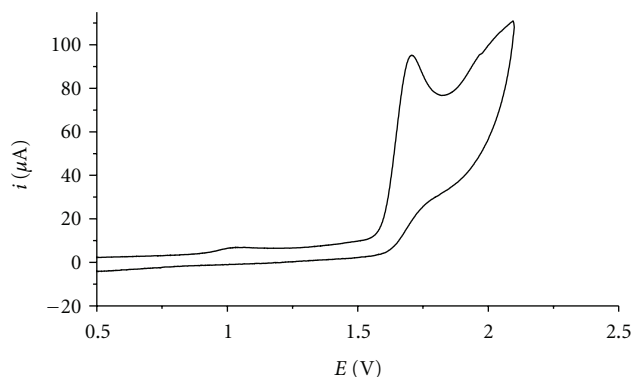


FIGURE 3: Oxidation voltammogram of *aclonifen*. Acetonitrile, $NBu_4BF_4$ 0.1 M, $C = 3$ mM, $v = 20$ mV s$^{-1}$, glassy carbon disk ($d = 3$ mm), reference: SCE.



FIGURE 4: *Aclonifen* potential peak variation with scan rate $C = 2$ mM, reference: SCE.

aromatic amine such as aniline and its derivatives, which are oxidized in the well-known polyaniline conducting polymer. For *aclonifen*, the ultimate oxidation product being an azo dimeric compound, the amino group is likely the preferred site for electron uptake and coupling. This explains why

the polymerization process is not actually observed. Thus, the mechanistic scheme of aclonifen oxidation involves very probably the steps given in Scheme 3. It accounts for the voltammetric, preparative, and coulometric results.

The cation radical (I) ensuing the first electron transfer is deprotonated in a rate determining step. The resulting radical (II) undergoes a rapid dimerisation and gives the intermediate (III), which is oxidized and deprotonated before leading to the final azo compound.
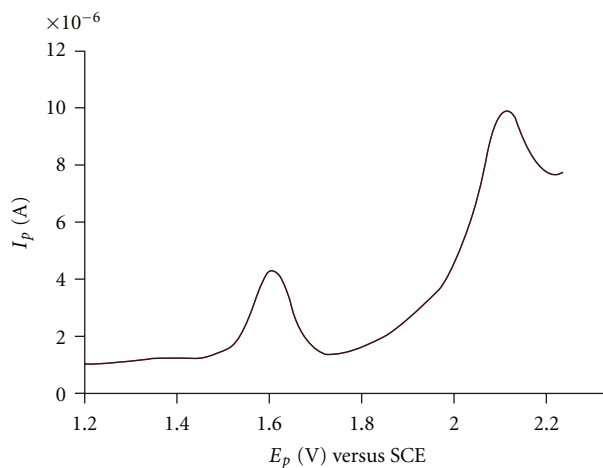
Figure 5: Differential pulse voltammogram of *aclonifen*. ($C$ = 15 ppm) and *bifenox* ($C$ = 15 ppm). Acetonitrile, Bu$_4$NBF$_4$ (0.1 M), glassy carbon ($d$ = 3 mm); scan rate: 5 mV s$^{-1}$; pulse amplitude = 50 mV; pulse width: 20 ms.
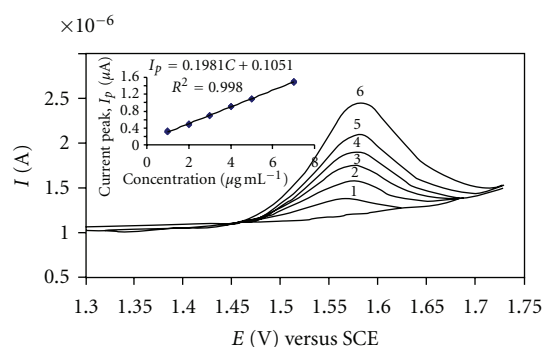


Figure 6: Differential pulse voltammograms of *aclonifen* in acetonitrile, Bu$_4$NBF$_4$ (0.1 M), glassy carbon ($d$ = 3 mm); scan rate: 5 mV s$^{-1}$; pulse amplitude = 50 mV; pulse width: 20 ms. $C$ = 1 − 7 $\mu$g/mL.

## 4. Analysis of *Aclonifen* Using Differential Pulse Voltammetry (DPV)

The results of the above electrochemical study of several herbicides can be used for their electrochemical determination. The present section concerns the determination of *aclonifen* by differential pulse voltammetry. The DPV analysis is preferred to cyclic voltammetry for quantification, since the developed peaks are better defined. The DPV anodic voltammogram on a glassy carbon electrode of *aclonifen* in the presence of *bifenox* is given in Figure 5.

Thus, a selective determination of *aclonifen* is possible in natural matrix containing both compounds. Figure 6 illustrates the DPV voltammograms obtained with *aclonifen* concentrations comprised in the range: 1–7 $\mu$g/mL.

The calibration plot of the peak current versus the concentration is linear ($R^2$ = 0.998). The limit of detection (LOD) and the limit of quantification (LOQ) calculated

according to the XTP 90–210 standard are, respectively, 0.6 and 0.8 $\mu$g/mL.

## 5. Conclusion

The electrochemical behaviour of five nitro diphenyl ether derivatives used as herbicides is investigated in acetonitrile on a glassy carbon electrode. On one hand, the cathodic reduction leads to the corresponding anion radical which is stable at the voltammetric scale, except *acifluorfen* which gives an irreversible cathodic peak. This is due probably to an intramolecular protonation of the nitroaromatic anion radical by the neighbouring acidic group. On the other hand, the studied herbicides give irreversible oxidation peaks. The number of exchanged electrons is superior to 2 except for *aclonifen*. A detailed study carried out for this compound shows that the predominant oxidation process involves a coupling step. Indeed the major oxidation product is an azo dimeric compound. A mechanistic scheme accounting for this result is proposed.

Furthermore, this electrochemical study shows that differential pulse voltammetry on a glassy carbon electrode is effective in the selective determination of *aclonifen* in the presence of *bifenox*. The corresponding limits of detection and quantification are obtained.

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