

THE EFFECT OF pH ON THE ELECTROCHEMICAL DEGRADATION
OF A GROUP OF UREA HERBICIDES

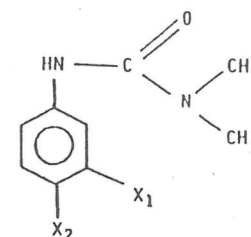
Ana M. Oliveira Brett and S. Ajao Adeyemi*

Departamento de Química, Universidade de Coimbra,
3049 Coimbra, Portugal

* Institute of Ecology, Obafemi Awolowo University, Ile-Ife,
Nigeria

Urea herbicides are some of the most widely used for weed control and, as for a large number of herbicides, they act as inhibitors of the photosynthetic electron flow by competitive binding [1]. The use of these chemicals in crop protection has had disastrous consequences in the biological equilibrium; not only pathogens and pests are destroyed but also many living organisms and plant species. These side effects are well recognised and it is important to understand the mechanisms of action and degradation of this type of compound. Some previous work on the electrochemical detection of these herbicides [2] made us interested in investigating the oxidation mechanism of this type of compound.

The herbicides studied are ureas of the type



with different X_1 and X_2 . Their commercial names are Fenuron ($X_1=H, X_2=H$), Diuron ($X_1=Cl, X_2=Cl$), Chlortoluron ($X_1=Cl, X_2=CH_3$), Fluometuron ($X_1=CF_3, X_2=H$).

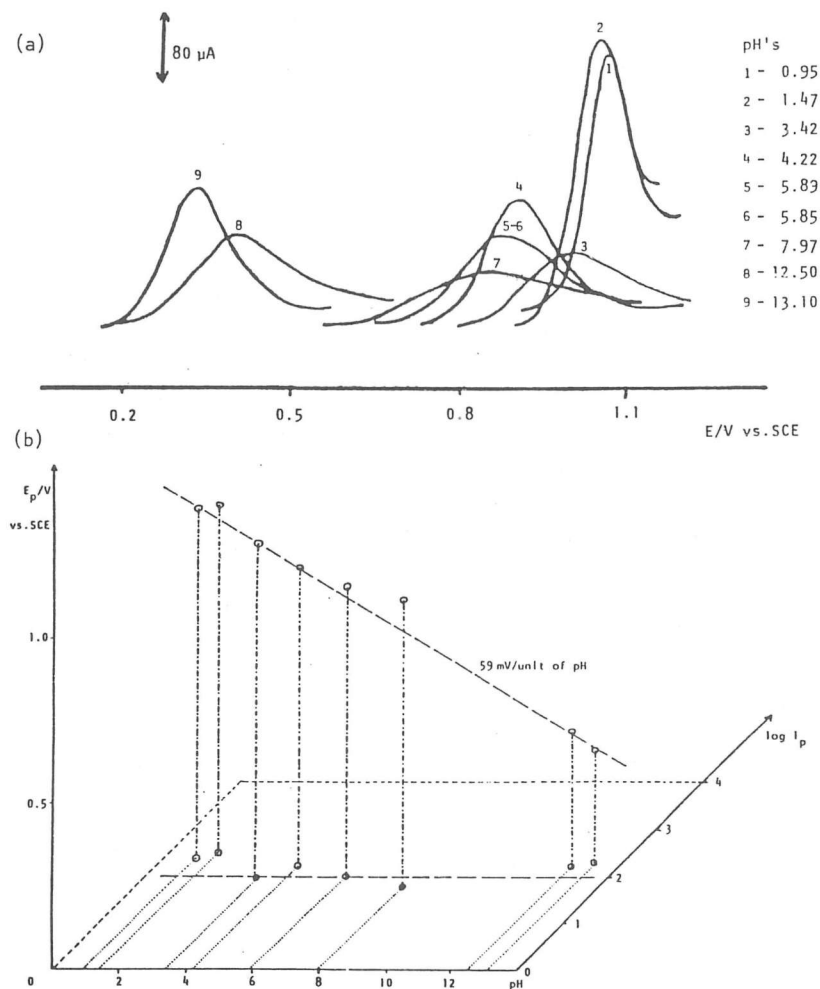


Fig 1 Results from differential pulse experiments with chlortoluron (concn. 5×10^{-4} mol dm^{-3}). Electrolyte: buffer + 5% ethanol. (a) Voltammograms (b) 3-D plot showing variation of peak potential, E_p , and $\log(\text{peak current})$, $\log i_p$, with pH.

Anodic oxidation of these compounds was studied over a wide range of pH (0.95 \rightarrow 13.10) at a stationary glassy carbon disc electrode in buffered aqueous media using differential pulse voltammetry. Cyclic voltammetry had already shown the complete irreversibility of the oxidation reaction.

In Fig. 1(a) we show differential pulse voltammograms for chlortoluron. The three dimensional plot in Fig. 1(b) shows the progressive change in the position of the oxidation peak with pH following a line of slope 59 mV/unit of pH suggesting a one electron transfer reaction. These are typical results for the group of herbicides studied. Fig. 2 shows the variation of peak potential with pH for all the herbicides of this study.

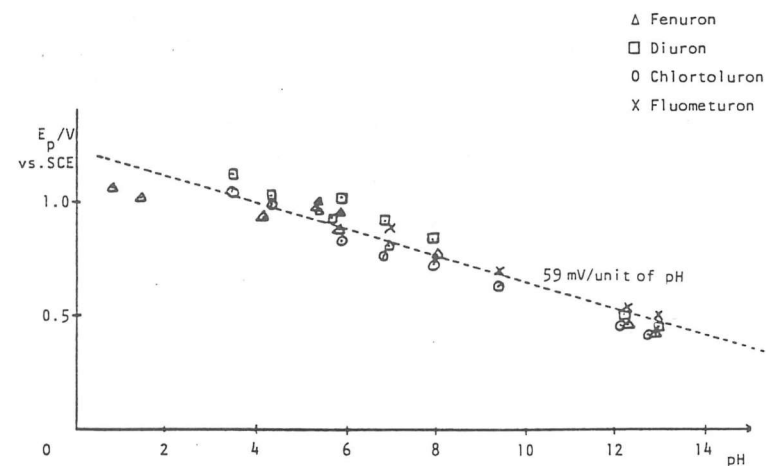


Fig. 2 Plot of peak potential, E_p , vs. pH from differential pulse voltammograms for all herbicides. Herbicide concn. 5×10^{-4} mol dm^{-3} ; electrolyte - buffer + 5 % ethanol.

More information may be obtained from analysing the shape of the differential pulse voltammograms. Measurement of the peak width at half-height of the differential pulse voltammogram, $W_{1/2}$, and use of the formula [3]

$$W_{1/2} = 3.52RT/nF$$

enables calculation of n , the number of electrons transferred. From our voltammograms we found values of n between 0.5 and 1.0 for the different herbicides. This result suggests a degradation mechanism that includes the formation of dimers at some pH's.

The anodic oxidation mechanism of these urea herbicides leads to various products. We have evidence that the final products are not electroactive and adsorb irreversibly at the surface of the electrode: this was confirmed by bulk electrolysis where there was total blockage of the electrode surface by the products. An HPLC analysis of the products of electrochemical degradation of Fenuron show three different compounds which we are trying to identify using i.r. and n.m.r. spectroscopy. Similar studies are being carried out with the other herbicides. However it seems that a plausible explanation is that the oxidation of these ureas herbicides forms a radical that may dimerise, polymerise or cleave.

References

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O₂ REDUCTION ON REORGANIZED GOLD SURFACES

Carlos Paliteiro

Departamento de Química, Universidade de Coimbra, Portugal

The reduction of O₂ on gold was shown to be structure dependent (1,2). The (100) surface reduces O₂ at a lower overpotential than the (110) and (111) surfaces; moreover, in alkaline solutions and at low overpotentials, the former surface is able to reduce O₂ to HO₂⁻ whereas the latter reduce O₂ only to HO₂⁻.

We found (3) that in alkaline solutions O₂ is reduced to HO₂⁻ on polycrystalline gold and on thin films of gold deposited on graphite and platinum. The polarization curves relative to O₂ reduction on the above mentioned surfaces show considerable hysteresis when recorded between -50 mV and ≈1270 mV (potentials are referred to the hydrogen electrode immersed in the same solution).

If however the potential is slowly scanned from -50 mV to ≈1000 mV in alkaline solutions, the shape of the polarization curves for both thin films and polycrystalline surfaces gradually change to the characteristic shape of the polarization curves of the (100) surface (Fig.1). This change is followed by a decrease of the hysteresis.

The cycled ("100") surface is stable out of the cell, both in pyrolyzed water and in air. It is also stable in acid solutions. In 10⁻² M HClO₄, we found the same relative activity for the "100" and the uncycled polycrystalline ("111") surfaces (Fig.2) as that reported by Jüttner (4) for the (100) and the (111) single crystal surfaces. The "100" face reverts to the "111" face when the potential is cycled