

POLAROGRAPHY OF SOME AROMATIC AND HETEROCYCLIC NITROSO COMPOUNDS

Inna AVRUTSKAYA and Michail FIOSHIN

Mendeleev Institute of Chemical Technology, Moscow, USSR

Received October 23rd, 1980

The electrochemical reduction of 4-nitrosodiphenylamine, 3-methyl-4-amino-5-nitrosouracil and 1,3-dimethyl-4-amino-5-nitrosouracil was studied in connection with the development of methods of electrosynthesis of some amino derivatives, intermediate compounds in the production of medicinal preparations and antioxidants of polymeric materials.

A single diffusion-controlled four-electron wave is observed in the polarograms of 4-nitrosodiphenylamine (*I*) at pH above 9 (at lower pH *I* is unstable) and concentrations below $5 \cdot 10^{-4}$ mol/l and of 3-methyl-4-amino-5-nitrosouracil (*II*) and 1,3-dimethyl-4-amino-5-nitrosouracil (*III*) and at pH from 1 to 7. By the method of cyclic voltammetry it was shown that such polarographic behaviour is explained by reduction of these compounds according to the E.C.E. mechanism¹⁻⁴.

RESULTS

On the voltammetric curves in the first cycle of voltage application at pH above 9 and voltage scanning rate lower than 0.16 V/s for *I* and in the entire pH range and at voltage scanning rates up to 50 V/s for *II* and *III* cathodic peaks are observed with potentials φ_p close to $\varphi_{1/2}$ of these compounds under similar conditions (Fig. 1). Beginning from pH 7 peaks of oxidation of the corresponding amino derivatives *I'*, *II'* and *III'* formed in the cathodic reaction appear with φ_p from -0.2 to 0.4 V depending on solution pH.

Upon repeated voltage application to the same drop in solutions with pH 7 another cathodic peak may be observed with φ_p close to φ_p of *I'*, *II'* and *III'*. This peak is presumably due to the reduction of products of *I'*, *II'* and *III'* oxidation. The oxidation products of 4-aminodiphenylamine (*I'*) and of substituted 4,5-diaminouracils (*II'* and *III'*) in a wide pH range and on various electrode materials are the appropriate imino derivatives: N-phenylquinone diimine (*I''*) and 4,5-diimino-uracils (*II''* and *III''*)⁵. The peaks of reduction of *I''*, *II''* and *III''* are displayed at potentials which are less negative by 0.4–0.6 V than the cathodic peaks of *I*, *II* and *III*.

At voltage scanning rates above 0.16 for *I* and 50 V/s for *II* and *III* another anodic peak appears which forms a cathode-anode system with reduction peaks of *I*, *II* and *III* and which is the oxidation peaks of the intermediate reduction product, the corresponding hydroxylamino derivative (*I*^{''}, *II*^{''} and *III*^{''}) (Fig. 2.). At voltage application rates of 1 V/s and higher the height ratio of the anodic peak of *I*^{''} and cathodic peak of *I* becomes equal to unity and independent of the voltage application rate (Fig. 3). The potential difference between the cathodic and anodic peaks is 0.028 V which is close to the corresponding value for a reversible electrochemical process with participation of two electrons. For *II* and *III* equality of anodic and cathodic peak heights is not observed even at voltage scanning rate up to 200 V/s.

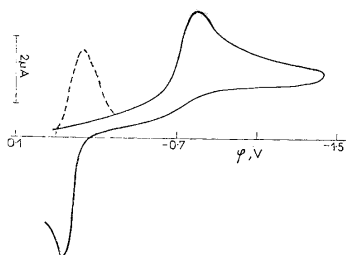


FIG. 1

Cyclic voltammogram of 3-methyl-4-amino-5-nitrosouracil (pH 9.2, 0.5 V/s, $6.25 \cdot 10^{-4}$ mol/l). Beginning of the second voltage application cycle is indicated by dashed line

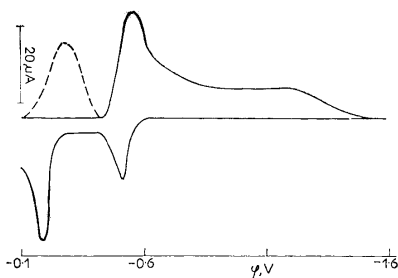
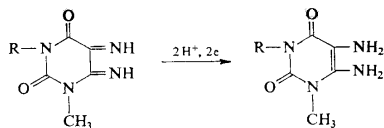
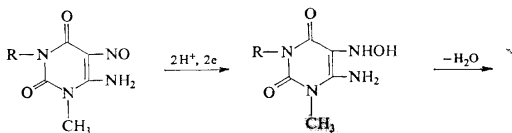
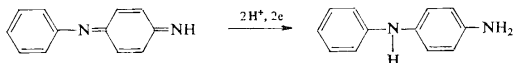
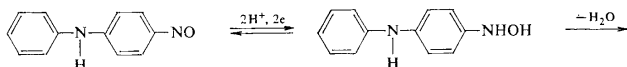


FIG. 2

Cyclic voltammogram of 4-nitroso-diphenylamine (0.1 mol/l NaOH, 1 V/s, $6.6 \cdot 10^{-4}$ mol/l). Beginning of the second voltage application cycle is indicated by dashed line

DISCUSSION

It may be assumed that reduction of *I*, *II* and *III* proceeds according to the following schemes:



The first electrochemical stage involves addition of two electrons and protons with formation of the appropriate hydroxylamino derivative which dehydrates yielding quinone imine which in its turn is reduced with participation of two electrons and protons into the amino derivative at potentials less negative by 400–600 mV as compared the the initial nitroso compound. For *II* and *III* the rate of the chemical stage is considerably higher as compared with *I*. The first electrochemical stage is potential-determining.

The rate of the chemical reaction is considerably affected by temperature. The peak of *I'''* oxidation appears at significantly higher voltage application rates: 0.16, 0.5, 1.0 and 4.0 V/s at temperatures of 20, 30, 40 and 60°C respectively.

Under certain conditions the single four-electron wave of *I* and *II* is separated into two and in the case of *III* even into three steps. According to data of preparative electrolysis and cyclic voltammetry at plateau potentials of all waves the same product is formed, the corresponding amino compound.

Division of the wave of *I* is not connected with variation of the proton-donor activity of the medium since the wave height ratio is independent of pH and buffer

capacity of the solution. Wave division occurs with increase of the concentration of I , the limiting current of the first step acquiring a kinetical character. At concentrations of I above $1.6 \cdot 10^{-2}$ mol/l the first wave again becomes diffusional its height, however, drops to the two-electron level (Fig. 4). Decrease of the four-electron

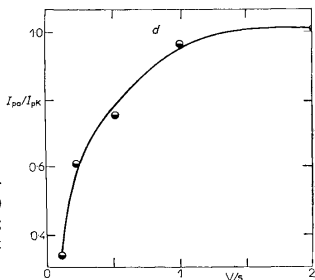
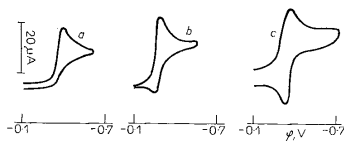


FIG. 3

Cyclic voltammogram of 4-nitrosodiphenylamine (0.1 mol/l) NaOH, $6.6 \cdot 10^{-4}$ mol/l) at voltage application rates: a 0.08; b 0.16; c 1 V/s and d the dependence of peak height ratio on voltage application rate

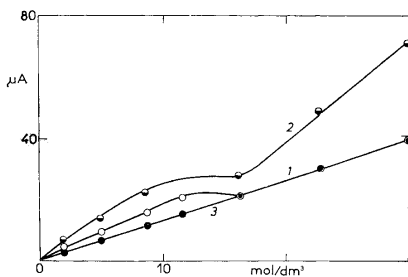


FIG. 4

Dependence of I_{lim} of the 1 first; 2 overall waves, and 3 of calculated value of I_{lim} for the two-electron process on 4-nitrosodiphenylamine concentration in the presence of 0.1 mol/l NaOH. Alcohol content 20% vol

wave of I reduction to a two-electron one is also observed at low concentrations when the end reduction product (I') or extraneous surfactants (e.g. camphor) are added to the solution. The region of potentials of the second wave beginning co-

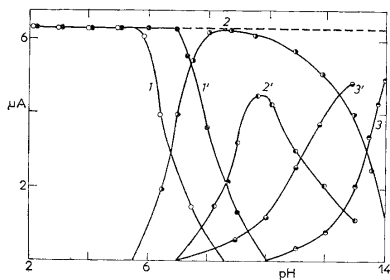


FIG. 5

I_{lim} vs pH dependence for 1, 1' the first; 2, 2' second; 3, 3' third wave of reduction of 3-methyl- and 1,3-dimethyl-4-amino-5-nitrosouracils

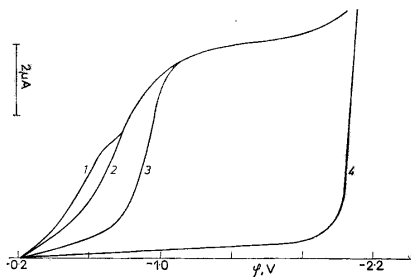


FIG. 6

Polarogram of 1,3-dimethyl-4-amino-5-nitrosouracil ($1.1 \cdot 10^{-3}$ mol/l 1 and with additions of 10^{-2} mol/l of 1,3-diethyl-4,5-diaminouracil 2 and of $1.7 \cdot 10^{-3}$ mol/l of camphor 3 at pH 8.4; 4 background curve

incides with the potential of camphor desorption, determined from the effect of the latter on the residual polarographic current. Therefore I' appearing as a result of reduction causes deceleration of the chemical reaction which follows reversible transfer of the first two electrons. At higher temperatures the observed effects disappear; this is explained by decrease in the surface activity of I' and by increase of the chemical reaction rate.

Wave division in the case of II and III is due to their acid-base properties. It is known that, uracils display weak basic properties and undergo protonation⁶.

Waves of II and III divide in the pH region of 7–8, while the overall wave retains its diffusional character. The wave height ratio depends on pH, buffer capacity and on concentration of II and III (Fig. 5). With increase of pH the first wave diminishes and at pH > 8.5–9.4 it disappears. Lowering of the concentration of ammonia buffer solution containing $1.4 \cdot 10^{-3} M$ of II or III to 0.01 mol/l results in wave separation which is absent in more concentrated solutions.

The UV spectra of II and III in the range of pH 1–7 display one absorption band with maximum at 315 nm indicating constancy of the nitrosouracil structure in the given pH range. Under these conditions they apparently exist in the form of neutral molecules. In 0.6 mol/l solution of sulphuric acid a new absorption band appears with maximum at 260 nm which presumably corresponds to the protonated form of the compounds studied. The band belonging to the neutral molecule is retained. In 3.75 mol/l solution of sulphuric acid uracils are present only in the protonated form.

The observed division of waves of II and III in the range of pH 7–8 may be associated with reduction of the protonated and nonprotonated forms of these compounds. Since the protonated form of nitrosouracils is absent in the solution bulk at these pH according to UV spectral data, under conditions of polarographic reduction surface protonation of the neutral molecule presumably takes place.

Study of the effect of reaction products on the polarographic behaviour of II and III shows that their addition to the solution leads to suppression of the first wave (Fig. 6). A similar effect is caused by extraneous surfactants, *e.g.* camphor. These additions do not affect the height of the overall wave.

Another wave appears at pH 11 for II and at pH 7 for III in the region of more negative potentials. With increase of pH the height of the more positive wave decreases and of the negative one increases. The overall current of both waves remains constant and is of diffusional nature. The more positive (second) wave has a kinetical nature.

The UV spectra of II and III in the region of pH 10–14 exhibit a new absorption band with maximum at 297 nm which apparently corresponds to the anions of II and III . The height of the more positive wave is evidently determined by the recombination rate of II and III anions into neutral molecules. For III in the region of pH 7.5–9.5 all three waves may be observed corresponding to reduction of the protonated form, the neutral molecule and the anion.

REFERNECES

1. Sarsenbaeva G. M., Avrutskaya I. A., Fioshin M. Ya.: *Elektrokhimiya* 13, 290 (1977).
2. Sarsenbaeva G. M., Avrutskaya I. A., Fioshin M. Ya.: *Elektrokhimiya* 14, 1861 (1978).
3. Dolgachev A. N., Avrutskaya I. A., Fioshin M. Ya.: *Elektrokhimiya* 15, 571 (1979).
4. Dolgachev A. N., Avrutskaya I. A., Fioshin M. Ya.: *Elektrokhimiya* 15, 1882 (1979).
5. Visinski B., Dryhurst G.: *J. Electroanal. Chem. Interfacial Electrochem.* 70, 199 (1976).
6. Joule J., Smith G.: *The principles of the Chemistry of Heretocyclic Compounds* (in Russian). Mir, Moscow 1975.