

POLAROGRAPHIC AND CYCLIC VOLTAMMETRIC REDUCTION OF *o*-CHLOROBENZALDEHYDE ISONICOTINOYLHYDRAZONE

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ABSTRACT

Polarographic and cyclic voltammetric studies of *o*-chlorobenzaldehyde isonicotinoylhydrazone were carried out in acid and alkaline solutions. The compound shows two polarographic waves in solutions of pH 2–9. In cyclic voltammetric studies, the hydrazone exhibits three cathodic peaks in acid solutions and two cathodic peaks in alkaline solutions. On the basis of these observations it is proposed that the compound undergoes reductive cleavage of =N–N–linkage, followed by the electrochemical reduction of the amide and the imine, the products of the cleavage, to alcohol and amine respectively.

POLAROGRAPHIC and cyclic voltammetric studies of carbonyl derivatives of isonicotinoylhydrazide were undertaken in view of their wide medicinal importance^{1,2}. The results obtained for *o*-chlorobenzaldehyde isonicotinoylhydrazone (*o*-Cl-BAINH) are reported here.

EXPERIMENTAL

The compound (*o*-Cl-BAINH) was prepared by the method reported in the literature³ and purified by repeated recrystallization from hot aqueous alcohol. The hydrazone was confirmed from infrared spectral data and melting point (observed value 222°C, corresponding to the value given in the literature, 221–222°C).

Current–voltage curves were recorded in Britton–Robinson buffer solutions (pH 2–9). A DC pen recording polarograph (model CL-25, ELICO Private Limited, Hyderabad, India) was used to record current–voltage curves. The dropping mercury electrode had the following characteristics: $t = 3.0$ S, $m = 1.93$ mg S⁻¹ at a height of 85 cm of mercury column in water under open circuit conditions. Cyclic voltammograms were recorded with a polarographic analyser (model 174 A, Applied Research Company, Princeton, USA) coupled with an X–Y recorder (model RE 0074) and Universal Programmer (model 175). Hanging mercury drop electrode (Metrohm model 9323), platinum wire electrode and SCE were used as working electrode, counter electrode and reference electrode respectively. The results are presented in tables 1 and 2 and figure 1.

RESULTS AND DISCUSSION

Electrochemical reduction in acid solutions

The hydrazone (*o*-Cl-BAINH) shows two polarographic waves in acid solutions. The limiting current

Table 1 Polarographic half-wave potentials of *o*-chlorobenzaldehyde isonicotinoylhydrazone
Medium, 20% aqueous DMF
[*o*-Cl-BAINH] = 4×10^{-3} M

| pH | – $E_{1/2}$ V vs SCE | |
|-----|----------------------|-------------|
| | First wave | Second wave |
| 2.0 | 0.75 | 0.87 |
| 3.0 | 0.82 | 0.97 |
| 4.0 | 0.87 | 1.02 |
| 5.0 | 0.92 | 1.08 |
| 6.0 | 0.99 | 1.16 |
| 7.0 | 1.07 | 1.20 |
| 8.0 | 1.14 | 1.26 |
| 9.0 | 1.18 | 1.29 |

Table 2 Peak potentials of *o*-chlorobenzaldehyde isonicotinoylhydrazone
Medium, 20% aqueous DMF
[*o*-Cl-BAINH] = 4×10^{-4} M

| Sweep rate V S ⁻¹ | – $E_{PC_{1s}}$ | – $E_{PC_{2s}}$ | – $E_{PC_{3s}}$ |
|---------------------------------|-----------------|-----------------|-----------------|
| pH 4.0 | | | |
| 0.050 | 0.89 | 0.99 | 1.24 |
| 0.100 | 0.91 | 1.00 | 1.25 |
| pH 8.0 | | | |
| 0.050 | 1.17 | 1.22 | |
| 0.100 | 1.18 | 1.30 | |

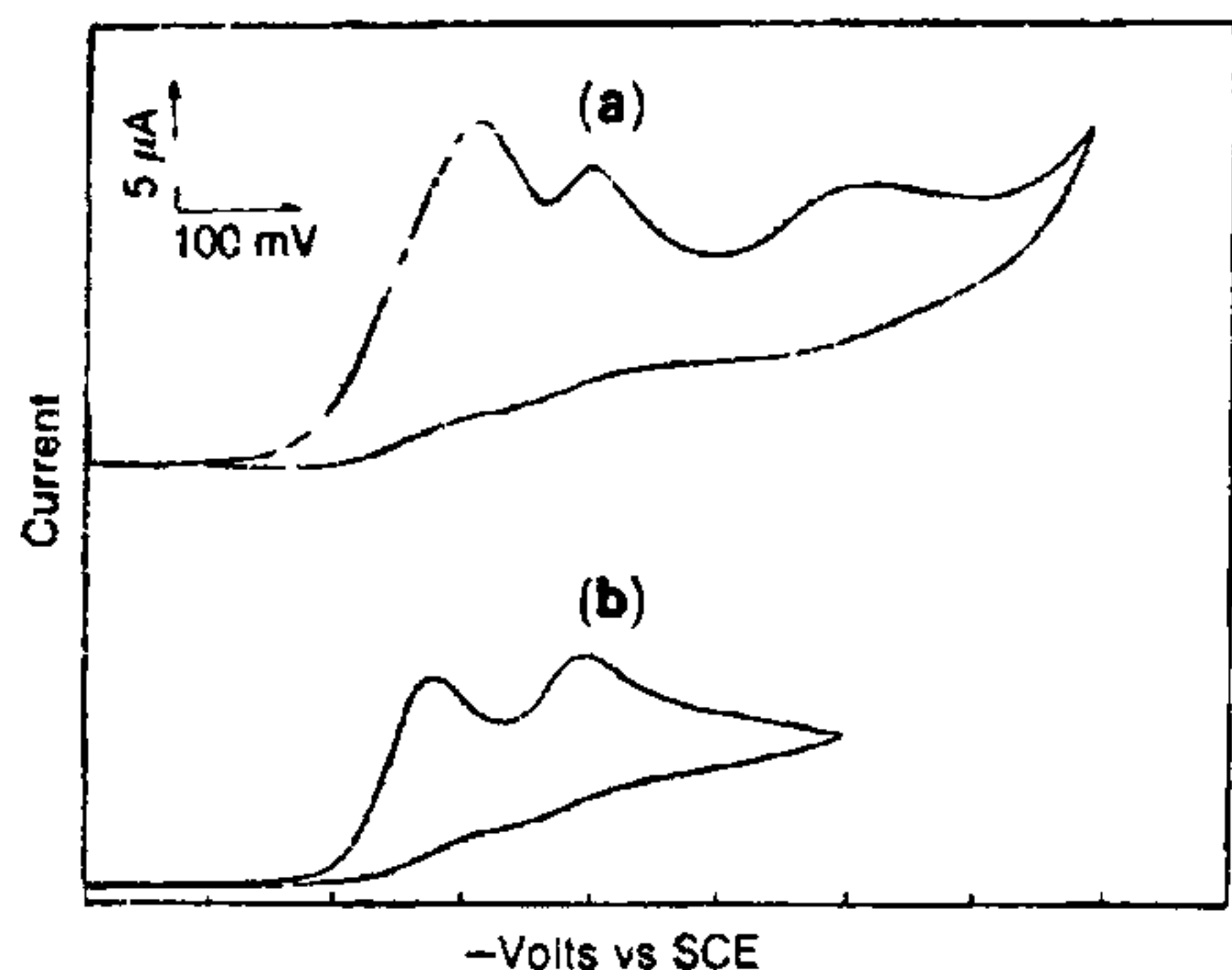


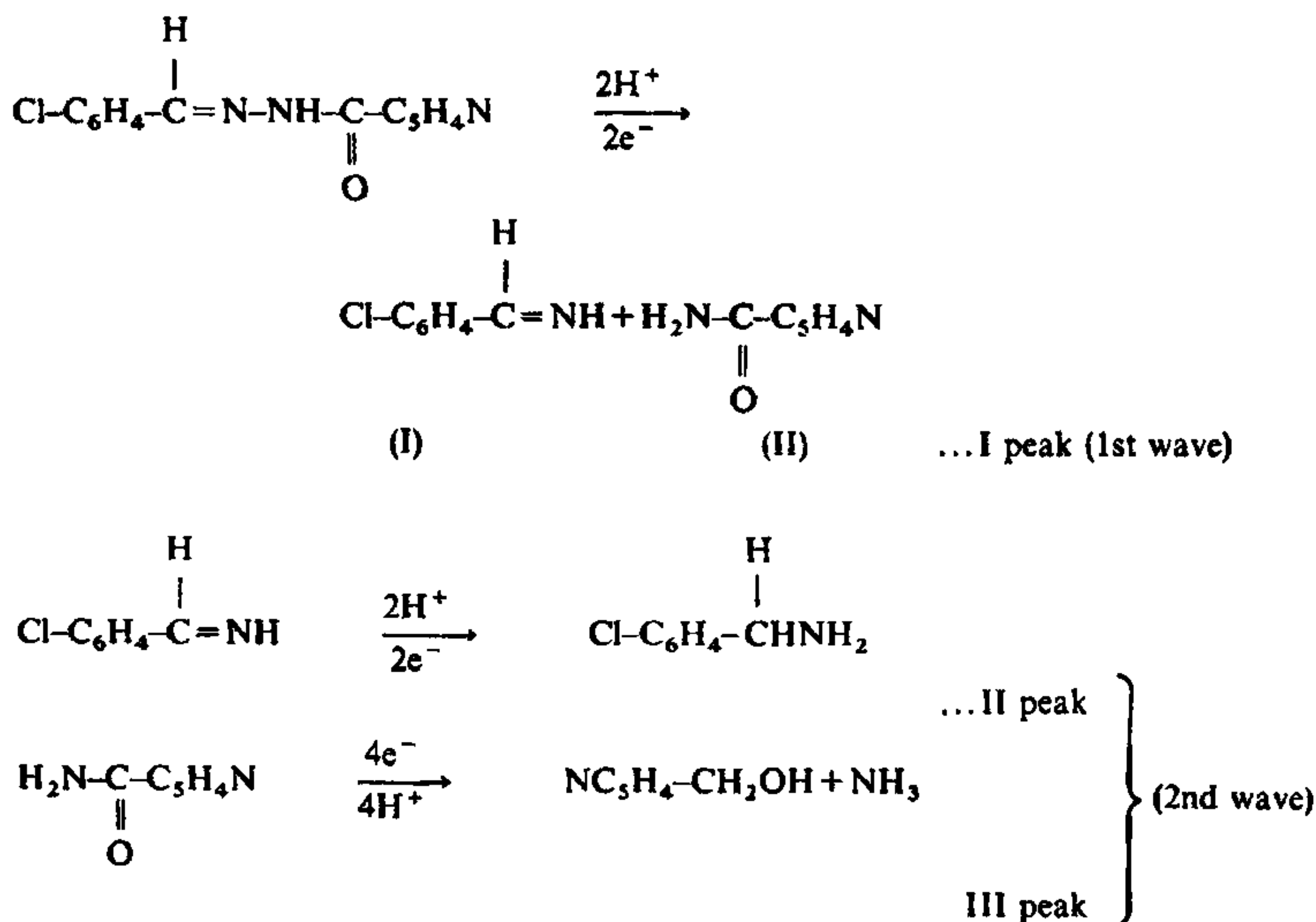
Figure 1. Typical cyclic voltammograms of *o*-chlorobenzaldehyde isonicotinoylhydrazone. a, at pH 4.0 (initial voltage, -0.6 V; sweep rate, 100 mV s^{-1}). b, at pH 8.0 (initial voltage, -0.9 V; sweep rate, 100 mV s^{-1}).

varied linearly with the concentration of the hydrazone and with the square root of the mercury column height, indicating that the wave is diffusion-controlled. The half-wave potential shifts towards more negative potentials with increase in concentra-

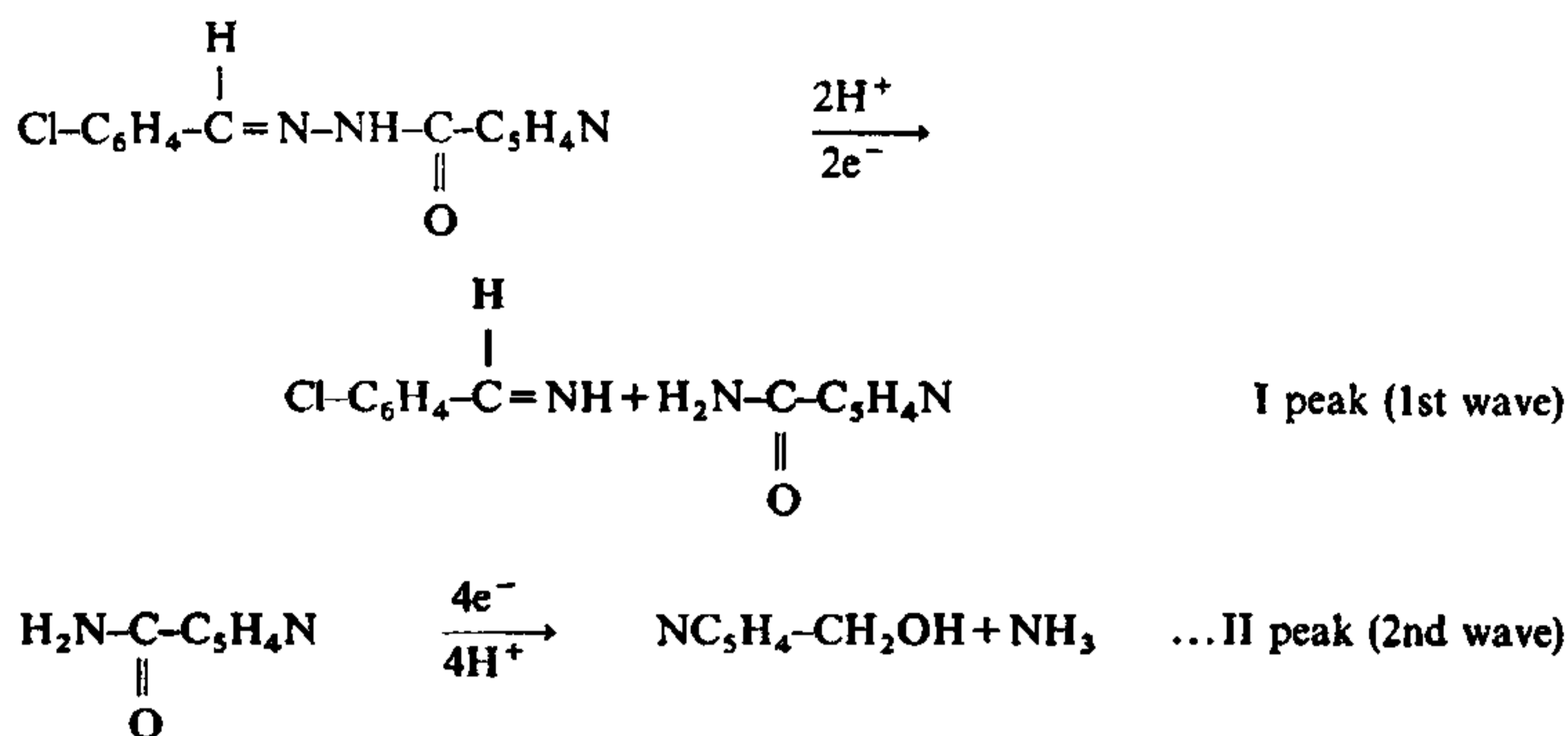
tion of the depolarizer, showing that the electrode process is irreversible. This is further confirmed by semilogarithmic analysis. The half-wave potential shifts towards more negative potentials with pH indicating that protons are involved in the reduction process.

The cyclic voltammogram of the compound shows three cathodic peaks in acid solutions in the forward scan; in the reverse scan no peak is observed. This indicates the irreversible nature of the electrode process. This is also confirmed by the negative shift in the peak potentials with increasing sweep rates.

The total number of electrons involved in the polarographic reduction process is established coulometrically to be two and six for first and second waves respectively. The first wave is attributed to the reductive cleavage of $=\text{N}-\text{N}-$ linkage involving two electrons. The second wave is attributed to the reduction of the imine and the amide to amine and alcohol respectively. The fact that a single wave is observed shows that the two reductions are taking place at almost the same potentials. This is in tune with the reported⁴ behaviour of semicarbazones (compounds bearing structural relationship with the present compound). For the purpose of product analysis bulk electrolysis was carried out. However



Scheme 1



Scheme 2

isolation of the products could not be carried out because of low yields. Therefore the catholyte was concentrated and extracted with ether and the extract was tested chemically for the functional groups. The extract gave positive tests for the primary amine (diazotization and coupling with β -naphthol) and for the primary alcohol (oxidation and condensation with 2,4-dinitrophenylhydrazine). The mechanism shown in scheme 1, is therefore proposed for the reduction of *o*-Cl-BAINH.

Electrochemical reduction in alkaline solutions

The hydrazone (*o*-Cl-BAINH) in alkaline solutions shows two polarographic waves. The waves are diffusion-controlled as indicated by the effect of mercury column height and concentration of the hydrazone on the wave height. Semilogarithmic analysis shows the wave to be irreversible. The compound shows two cathodic peaks in the forward scan of the cyclic voltammogram; in reverse scan no peak is observed. This suggests that the electrode process is an irreversible one. This is further confirmed by the negative shift in the peak potentials with increasing sweep rates.

It was reported in the literature that the imine formed during the reductive cleavage of =N-N-linkage in semicarbazones is resistant to further reduction⁵. Further, the reduction of the imine takes place only in the protonated form. The absence of imine reduction wave in alkaline solution is therefore attributed to a significant decrease in the recombination rate. It was reported that amides undergo reduction to the corresponding alcohols⁶. The formation of alcohol as well as the aldehyde in alkaline solutions was confirmed by bulk electrolysis

and subsequent identification. The aldehyde formed is attributed to the decomposition of Ar-CH=NH to Ar-CHO in alkaline solutions. The first wave thus represents the =N-N- reductive cleavage and the second wave the reduction of the amide. The fact that the protonated amide is susceptible to the reduction substantiates the shift in half-wave potential towards negative values in alkaline medium. The observation of two peaks in cyclic voltammograms at potentials equal to the polarographic half-wave potentials supports the mechanism proposed for the polarographic reduction (scheme 2).

1 March 1988

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