INVESTIGATION OF THE MECHANISM OF THE
POLAROGRAPHIC REDUCTION OF THE SYDNONEIMMONIUM
CATION

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The polarographic reduction of the sydnoneimmonium cation (I) was investigated in the case of 3-β-phenylisopropylsydnoneimine hydrochloride (sydnophen). The effect of the pH, alcohol concentration, ionic strength, and surface-active substances was studied, and the electrolysis was carried out at a controllable potential under various conditions. The cyclic voltamperograms were recorded. A mechanism for the reduction of I is proposed. Cleavage of the ring of I in the near-electrode space is observed in unbuffered media. The first direct proof of the existence of the unstable sydnoneimine base was obtained.

Sydnoneimines constitute a pseudoaromatic system and are classified as so-called mesonionic heterocyclic compounds. The aromatic sextet in mesonionic heterocycles is realized by partial ejection of one of the seven 2pz electrons of the ring to the "exocyclic group" (for example, the oxygen atom in sydrones) or by complete ejection of the electron to the anion (as in sydnoneimine salts). It has been established that sydrones [1-3] and sydnoneimine salts [4] are capable of reduction on a dropping mercury electrode. The mechanism of the reduction of sydrones in aqueous alcohol media is determined by the pH of the medium: N-substituted α-amino acids are formed in acidic media with the consumption of six electrons, whereas four electrons participate in the neutral and alkaline media, and the reaction products are the corresponding substituted hydrazine-α-carboxylic acids [1-3]. Preliminary assumptions regarding the mechanism of the reduction of sydnoneimines have been expressed [4]. Inasmuch as 3-α-alkyl- and 3-alkylsydnoneimines undergo the same type of reduction [4], we selected 3-β-phenylisopropylsydnoneimine hydrochloride (I) for a more detailed study of the polarographic behavior of this class of compounds. This choice is also determined by the fact that I is a psychotropic medicinal preparation (sydnophen) [5] and is the starting material in the synthesis of another preparation — sydnocarb [6].

The study of the polarographic behavior of I was carried out in aqueous and aqueous alcohol buffered and unbuffered media with pH < 7, inasmuch as the sydnoneimine base (II) formed in alkaline solutions is extremely unstable and is readily converted, with ring opening, to the N-nitroso derivative of the nitrile of an N-substituted α-amino acid (III) [7, 8].

A single distinctly expressed wave is observed in the reduction of I in buffered media containing 10% ethanol over the entire investigated pH range. At pH > 3, the discharge current of the base electrolyte is shifted to positive potentials as the concentration of I increases, and this is apparently associated with catalytic hydrogen evolution, inasmuch as the catalytic current falls as the buffer capacity of the solution and the proton concentration decrease. An increase in the percentage of the organic solvent (ethanol) also has the same effect, and this is characteristic for processes that are limited by the rate of the antecedent protonation reaction [9].

The magnitude of the $E_{1/2}$ value of the reduction wave of I is independent (Fig. 1) of the pH ($E_{1/2} = -0.88$ V for solutions containing 10% ethanol). This is apparently associated with the fact that the sydnoneimmonium cations (I) are extremely weak acids and the $I \equiv II + H^+$ equilibrium is shifted practically
completely to favor I over the investigated pH range. However, the addition of a second proton to monocation I was not observed even in concentrated acids [10].

The limiting current increases somewhat as the pH increases from -1.0 to 1.0. It again begins to decrease as the pH is increased further and takes on an almost constant value at pH > 4 (Fig. 1).

At all of the pH values the limiting current depends linearly on the concentration of I, and an increase in the percentage of ethanol from 10 to 50% in 0.1 N HCl and in a buffer solution with pH 6.75 leads to a decrease in the height of the wave in conformity with the change in the viscosity of the medium: \( I_{\text{lim}} \eta^{1/2} = \text{const} \). From this it can be concluded that the limiting current has diffusion character in all of the investigated media.

In all likelihood, the reduction of I takes place in the adsorbed state. As the alcohol concentration increases, the adsorbability of I decreases, a first-order maximum develops on the wave, and the \( E_{1/2} \) value is shifted to negative potentials; however, the latter effect is small, inasmuch as it may be compensated to a certain degree [11] by an increase in the activity of cation I.

Coulometric measurements in a buffer solution with pH 6.1 (10% ethanol) give \( n = 4.2 \pm 0.1 \), whereas \( n = 5.1 \pm 0.1 \) during electrolysis in 0.1 N HC104 in 10% alcohol. This result is in agreement with the ratio of the heights of the waves of reduction of I at pH 6.1 and in 0.1 N perchloric acid. An anode wave (\( E_{1/2} = +0.03 \) V) is observed on the polarogram after electrolysis of I at pH 6.1, whereas the products of electrolysis of I in acidic media are incapable of oxidation on a mercury electrode. An anode peak similarly appears during voltamperometry with triangular imposition of the pulse in neutral medium, whereas the anode peak is absent in acidic media (Fig. 2).

We turned our attention to the fact that a new small wave (this is shown in the case of the buffer solution with pH 4.8, 10% ethanol) appears in addition to the wave of reduction of I at more negative potentials (\( E_{1/2} = -1.32 \) V when \( \mu = 0.1 \)) as the buffer capacity decreases considerably. In unbuffered aqueous KCl solutions this wave is expressed considerably more distinctly. Its height increases appreciably as the ionic strength of the solution increases (Fig. 3) and does not change with time. This phenomenon can be explained as follows. Inasmuch as the reduction of I is accompanied by the consumption of protons, alkalization of the near-space should occur in solutions with low buffer capacities and, especially, in unbuffered media; the alkalization effect should increase as the ionic strength increases as a result of a decrease in the \( \phi^+ \) potential [11]. Considering the instability of sydnoneimines in alkaline media, it can be assumed that partial opening of the sydnoneimine ring of I to give nitrosonitrile III occurs in the near-electrode space, and the wave at more negative potentials corresponds to the reduction of III. In fact, the addition of an equimolecular amount of NaOH to an unbuffered solution of I leads [7, 8] to disappearance of the wave of reduction of I with the simultaneous appearance of a wave of reduction of nitrosonitrile III, the \( E_{1/2} \) value of which corresponds to the \( E_{1/2} \) value of the second wave that appears in unbuffered media. The wave of reduction of nitrosonitrile III formed by the addition of alkali to a solution of I is half the wave of reduction of starting I, and the \( E_{1/2} \) value of III is independent of the alkali concentration. Acidification of the alkaline solution with excess mineral acid, as one should have expected [12], led to quantitative cyclization of III to I.

Fig. 1. Dependence of \( I_{\text{lim}} \) (1) and \( E_{1/2} \) (2) for the reduction of I on the pH (in 10% ethanol).

Fig. 2. Cyclic voltamperograms of I in 10% ethanol (0.5 V/sec): A) in 0.1 M HC104; B) at pH 6.16; 1) base electrolyte; 2) 0.3 mM I.