ELECTROCHEMICAL REDUCTION OF N-NITROAMINOTETRAZOLES

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The electrochemical reduction of 5-nitroamino- and 2-methyl-5-nitroaminotetrazoles at the first wave potential consumes six electrons, while the reduction at the second wave potential consumes eight or nine electrons. The preparative reduction of 2-methyl-5-nitroaminotetrazole at the second wave potential leads to 2-methyl-5-aminotetrazole and ammonia. A mechanism is proposed for these reactions.

A six-electron reduction wave is observed in the electrochemical reduction of aromatic and aliphatic N-nitroamines leading to substituted hydrazines [1, 2]:

$$\mathrm{RNHNO_2} \xrightarrow[6H^+]{6e^-} \mathrm{RNHNH_2} + 2\ \mathrm{H_2O}$$

In contrast, two reduction waves, which alternate upon change in the acidity of the medium, are observed in the reduction of primary N-nitroaminotetrazoles [3]. However, it has not been clear whether the limiting currents of these waves are diffusional or kinetic. Also, the number of electrons participating in the reduction of N-nitroaminotetrazoles at the first and second wave potentials as well as the reaction products have remained unknown.

The limiting currents of both waves proved diffusional in the pH ranges, at which they have their maxima. Thus, the activation energy of the limiting currents are 7.37 kJ at pH 3.06 for 5-nitroaminotetrazole (I) and 8.08 kJ at pH 0.20 and 9.36 kJ at pH 3.94 for 2-methyl-5-nitroaminotetrazole (II). The slopes of the i—t curves in the first drop in logarithmic coordinates (α) are 0.20-0.22. Kinetic limitations to the current appear in the segments characterized by a decrease in the limiting currents (α 0.25-0.33). The kinetic nature of the limiting current in the region characterized by a decrease in the first wave and increase in the second wave was also indicated by voltamperometry. The voltamperometric curves show two peaks, corresponding to the first and second waves on the polarographic curves. The ratio of the height of the first peak to the height of the second peak changes with increasing rate of potential application. The first peak disappears completely with a further increase in this rate. Such an effect may occur only if there are two forms of the nitroaminotetrazoles in equilibrium with each other. In the case of a stepwise reduction mechanism, the magnitude of the first peak cannot decrease below some level such as the one-electron level. In previous work [3], we proposed that the protonated and unprotonated forms are the equilibrium nitroaminotetrazole forms. The protonated forms are reduced in more acidic media (first wave), while the unprotonated forms are reduced in less acidic media (second wave).

Coulometric studies have shown that six electrons are consumed in the reduction of I and II at the first wave potentials. By analogy with previous results [1, 2], we may assume that 5-hydrazino- and 2-methyl-5-hydrazinotetrazoles are formed in this reduction.

Comparison of the limiting currents of the first and second reduction waves and the coulometric results suggest that eight or nine electrons are consumed in the reduction of I and II at the second wave potentials (the experimental precision does not permit an unequivocal determination of these values). There are no data in the literature on the reduction of N-nitroamines involving eight or nine electrons. In order to identify the reaction products, we carried out the preparative reduction of II at

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the second wave potentials. The reaction products are 2-methyl-5-aminotetrazole (III) and ammonia. The amount of ammonia produced is 1 mole per mole II. We should note that no ammonia production is noted in the preparative reduction of I and II at the first wave potentials.

These results indicate the following general scheme for the reduction of N-nitroaminotetrazoles at second wave potentials:

$$\mathrm{RNHNO_2} \xrightarrow[8H^+ \text{ or } 9H^+]{8e^- \text{ or } 9e^-} \mathrm{RNH_2} + \mathrm{NH_3} + 2\ \mathrm{H_2O}$$

These results are not trivial since the electrochemical reduction of N-nitroamines to give amines and ammonia had not been observed previously.

Two hypothetical reaction schemes may be proposed depending on whether the number of electrons participating in the reduction is eight or nine. In the eight-electron reduction mechanism, the first step is the two-electron reduction of II to amine III and nitrous acid. Further reduction of nitrous acid to give ammonia may occur in acid media [43] [sic].* This reaction may proceed according to the following scheme:

$$\mathrm{II} \xrightarrow[2H^+]{2e^-} \mathrm{III} + \mathrm{HNO_2}$$

$$\mathrm{HNO_2} \xrightarrow[6H^+]{6e^-} \mathrm{NH_3} + 2\ \mathrm{H_2O}\ .$$

The first step in the nine-electron reduction mechanism is the two-electron reduction of II to 2-methyl-5-nitrosoaminotetrazole (IV). The second step is the two-electron reduction of nitrosoamine IV to amine III and NO. Then, NO may be reduced in acid media to ammonia [5, 6] according to the following scheme [6]:

$$\mathrm{II} \xrightarrow[2H^+]{2e^-} \underset{\mathrm{IV}}{\mathrm{MeN_4CNHNO}} + \mathrm{H_2O}$$

$$\mathrm{IV} \xrightarrow[1H^+]{2e^-} \mathrm{III} + \mathrm{NO}$$

$$\mathrm{NO} \xrightarrow[6H^+]{5e^-} \mathrm{NH_4^+} + \mathrm{H_2O}$$

EXPERIMENTAL

The polarographic studies were carried out on an ON-102 instrument on a dropping mercury electrode with parameters m 1.547 mg/sec, τ 0.25 sec, and 50 cm mercury column height. A normal calomel electrode was the reference. The microcoulometric studies were carried out on an ON-102 instrument in a potentiostatic mode. The voltamperometry and recording of the i—t curves were carried out on an OP-3 oscillographic polarograph. The pH values of the acetate and citrate—phosphate buffer solutions were monitored by a pH-340 pH-meter. The ionic strength of the solutions was brought to 1.0 by adding sodium sulfate. In the preparative reduction, bottoms mercury (S 133 cm^2) was used as the cathode and a lead plate (S 200 cm^2) was used as the anode. The cathodic and anodic spaces were separated by a cellophane membrane. A normal calomel electrode was used as the reference. The anolyte was 1 N sulfuric acid. The concentration of the N-nitroamine in the catholyte was 5-10 moles/liter. The constant potential was maintained to within ±10 mV.

Determination of the Number of Electrons (n) Participating in the Reduction of I and II. In the case of I, coulometry was used to find n = 5.74 and 5.91 (at reduction potential −0.76 V and pH 0.41) and 8.46 and 8.68 (at reduction potential −1.30 V and pH 2.76). Comparison of the limiting currents of the first and second reduction waves indicated n = 8.93 and 8.81 (assuming similar values of the diffusion cases in these two cases).

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*The reference should probably be [3, 4] since the previous reference is [1, 2] and the following reference is [5, 6].

In the case of II, coulometry gave n = 6.14 and 5.89 (at reduction potential −0.72 V and pH 0.41) and 8.15 and 8.54 (at reduction potential −1.40 V and pH 4.0). Comparison of the limiting currents of the first and second reduction waves gave n = 8.73 and 8.61 (assuming similar diffusion coefficients in the two cases).

Preparative Reduction of I and II. After the preparative electrolysis of I and II at the first wave potentials, the reaction solution gives a negative test with the Nessler reagent (qualitative determination for ammonia). After the preparative electrolysis of II at the second wave potential, a positive test was obtained with the Nessler reagent. For the quantitative determination of ammonia, the reaction mixture was filtered and NaOH was added to the filtrate to bring the pH to at least 14. Ammonia was distilled into a sulfuric acid solution. The determination gave 79.5 and 103.5% mole NH_3 per mole II (at reduction potential −1.40 V and pH 4.0). In order to separate III, the solution after distilling off ammonia was acidified by the addition of hydrochloric acid to pH 1.0 and evaporated to dryness. The residue was extracted with ethanol. The solvent was removed and the dry residue was sublimed in vacuum at 120°C to give III, mp 102-103°C (103-104°C [7]).

The elemental analysis data for nitrogen corresponded to the calculated values.

REFERENCES

1. M. Baizer (ed.), Electrochemistry of Organic Compounds [Russian translation], Mir, Moscow (1976), p. 252.
2. E. Laviron, P. Fournazi, and J. Greusard, Bull. Soc. Chim. France, No. 4, 1255 (1967).
3. A. G. Mayants, V. S. Klimenko, V. V. Erina, K. G. Pyreseva, S. S. Gordeichuk, V. N. Leibzon, V. S. Kuz'min, and Yu. N. Burtsev, Khim. Geterotsikl. Soedin., No. 8, 1067 (1991).
4. N. E. Khomutov and U. S. Stamkulov, Moscow Chemical Engineering Institute, Moscow (1984); Dep. VINITI, June 13, 1984, No. 3900-84.
5. I. Paseka and J. Vonkova, Electrochim. Acta, **25**, 1251 (1980).
6. T. A. Kryukova, S. I. Sinyakova, and T. V. Aref'eva, Polarographic Analysis [in Russian], Khimiya, Moscow (1959), p. 386.
7. R. A. Henry and W. G. Finnigan, J. Am. Chem. Soc., **76**, 923 (1954).