

Short Communication

Mechanism of Cupferron Electroreduction

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Abstract- Detailed mechanism of cupferron electroreduction can be judged only on the parameters of kinetics of the reduction process, and on final products established. No stable intermediates were obtained or detected till now. The mechanism suggested earlier by Kolthoff and Liberti (1948) is logically acceptable, but it includes some intermediates with doubtful stability. Analysis of published data on reduction kinetics of some substances closely related to cupferron allowed to make a supposition that diazonium cation can be a reasonable intermediate in this process.

Keywords- Cupferron, Electroreduction, Reduction mechanism, Dropping mercury electrode, Phenyldiazonium

1. INTRODUCTION

Cupferron is an ammonium salt of N-nitroso-N-phenylhydroxylamine (NPHA). Four electrons are consumed in alkaline and six electrons in acidic media for its electroreduction; extensive protonation occurs during this process. Kinetic data derived from polarograms of cupferron can reveal only the starting stages of this reaction. Nevertheless, using kinetic data on reduction of some analogous substances or probable intermediates, it may be possible to elucidate detailed mechanism of cupferron reduction. For instance, such an analysis was performed in the case of nitro and nitroso compounds in excellent work by Zuman et al. [1], based on their own experimental results. Without any intention to make such a profound

work, some aspects of cupferron reduction can be compared with published data available on analogous substances, N-nitrosamines and hydroxylamine derivatives. It may help to answer some questions regarding the detailed mechanism of the process discussed.

2. DISCUSSION

2.1. Polarographic behavior of cupferron

Electroreduction of cupferron has been widely investigated [2-9]. Cupferron polarogram is traditionally described as having three polarographic waves [3], but this statement is misleading. Only two of the waves may be observed simultaneously at certain pH, but usually the only wave is found. You never could see all the three waves together. It would be better to say that there are three pH regions where cupferron wave has different parameters, or those parameters depend on pH in different way. The waves observed in these pH regions were numbered earlier consecutively from the lower pH to higher.

The first region is approximately pH 0-4. Elving and Olson supposed that polarographic wave of NPHA in strong acidic solutions is affected by tautomeric equilibrium [3]. But it is more likely that the wave in the most acidic media is due to reduction of protonated NPHA [9].

The second region is pH 4-7. According to [2,3], in acidic media total process of cupferron reduction is:

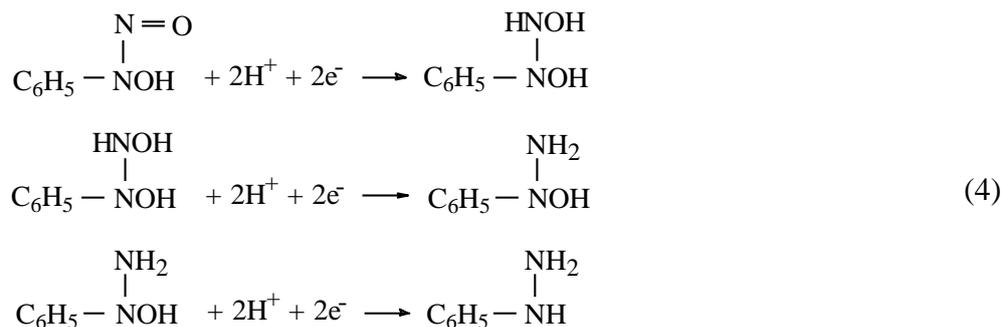


Kinetic analysis shows that prior protonation with adsorption of NPHA formed takes place before slow electrochemical step [9]:



Equation (3) describes a slow electron transfer (rate limiting step) only, further reduction results in the phenylhydroxylamine formation.

Kolthoff and Liberti suggested that the cupferron reduction proceeds through three two-electron sequential reactions [2]:



A similar mechanism has been proposed in [10] for the chemical reduction of cupferron by zinc amalgam.

In alkaline media (pH 8-10) overall process is [3]:



Kinetics of reduction is consistent with slow transfer of the first electron without preceding protonation.

In pH regions where two waves coexist (pH~4 and pH~8) kinetic currents have been observed due to slow protonation [3,7,8].

2.2. Cathodic reduction of compounds related to NPHA

From a formal point of view NPHA molecule has two functional groups capable of reduction, nitroso and hydroxylamine fragments. It is of interest to consider the kinetics of electroreduction of compounds having the most similar structure of electroactive groups, such as nitrosamines, hydroxylamines, etc. in order to elucidate complete reduction mechanism of cupferron.

Surely, there should be electronic interaction between the groups in a cupferron anion. X-ray analysis of cupferronates shows that bond lengths in NPHA anion differ significantly from the values corresponding to their formal multiplicity, indicating intensive electron interaction within the entire anion [11,12]. So it may be hard to find a proper model compound with electrochemical properties similar to cupferron.

Aliphatic or aromatic nitrosamines give four-electron reduction polarographic wave with the pH dependent half-wave potential in acidic medium and two-electron wave in an alkaline medium with $E_{1/2}$ independent on pH. The wave in acidic solutions corresponds to the reduction of the protonated nitrosamine; the protonation may be a limiting step, causing kinetic limiting current [13-15]. This behavior is very similar with cupferron reduction.

Kinetic currents of some nitrosamines were studied in [16,17]. Protonation reaction with first order in hydrogen ion was found. Calculation of the rate constant, without taking into account the adsorption of reactant, leads to abnormally high values theoretically invalid for a

bimolecular reaction. The authors concluded that the protonation of nitrosamines occurs in the adsorbed state. Surface nature of cathodic waves has been supported by the adsorption studies of nitrosamines at a mercury electrode [16-18].

It should be noted that in the case of cupferron reduction no apparent violation of the traditional concept of reaction layer was found [3]. Presumably, this is due to different adsorbability of unprotonated species, neutral nitrosamine molecules and anions of cupferron. In alkaline solutions kinetics of cupferron reduction is notably hindered compared to nitrosamines. The waves of the later compounds are more negative by 0.1–0.15 V [16-18]. The calculated slopes of semi-log plots are $b=80/103$ mV for aliphatic and $38/47$ mV for aromatic nitrosamines [19], they are significantly lower than $b \approx 130$ mV found for cupferron. Surprisingly low values of b for aromatic nitrosamines close to 40 mV are the most important, as they may imply reversible transfer of the first electron with slow transfer of the second one. It has been shown that aromatic nitrosamines (unlike aliphatic) can give well-defined peak with a half-width of 7-85 mV on differential-pulse polarograms [20]; this is consistent with reversible transfer of some electrons during reduction.

It is evident that introduction of hydroxyl group in cupferron dramatically reduces the stability of the particles, resulting from the transfer of the first electron per depolarizer molecule, and it does not allow reversible proceeding of this stage. But it should be noted that nitroso derivatives of secondary amines were taken for comparison (as it was inevitable), and the number of alkyl or aryl side chains can surely influence kinetics of electroreduction.

Comparison of electroreduction kinetics of cupferron and nitrosamines in acidic solutions gives similar results. No great difference in $E_{1/2}$ values is observed, but slopes of semi-log plots of cupferron waves (~ 180 mV) are much larger than values for aliphatic (82-120 mV [17], 50-100 mV [19]) and aromatic nitrosamines (35-45 mV [19]). The b values for latter also imply reversible transfer of the first electron, as in alkaline media.

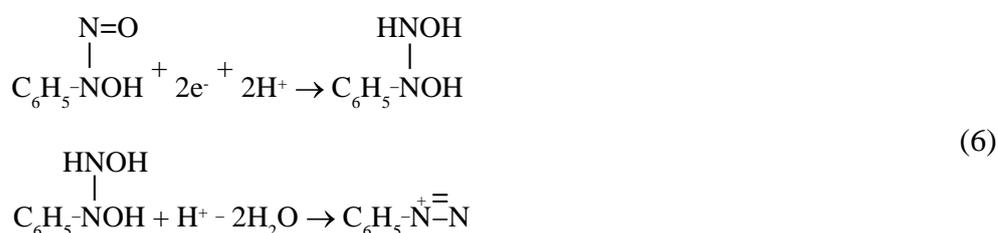
It can be concluded that reduction kinetics of cupferron and nitrosamines is similar in many aspects, but their reduction proceeds via different mechanisms. But one has to expect some similarity at the earliest stages, even if their rate is different enough. Without this similarity, it would be hard to record similar (in many aspects) kinetic waves of cupferron and nitrosamines.

If we consider hydroxylamine derivatives as cupferron analogs, we should closer look on hydroxamic acids, as they contain powerful electron accepting group as nitroso group in cupferron is. Simple compounds such as acetohydroxamic and propionhydroxamic acids reduce at extremely high negative potentials, $E_{1/2} < -2$ V [21,22]. But N-aryl-substituted hydroxamic acids may be much better model substance for comparison with cupferron. Unfortunately, it seems that no electrochemical data is available for such compounds. For instance, N-benzoyl-N-phenyl-hydroxylamine is a common analytical reactant, and a broad range of its metal complexes has been studied by polarography; but it seems that this

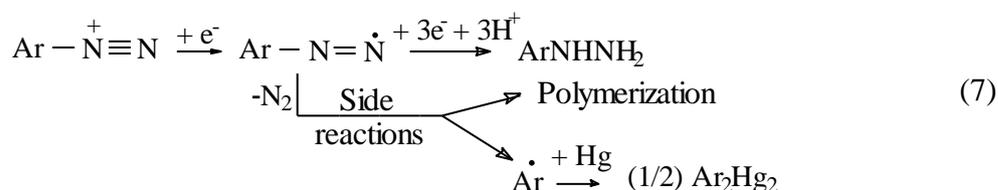
substance alone has been never investigated electrochemically. Anyway, it may be concluded that hydroxylamine moiety is presumably not the most electroactive part of NPHA molecule, at least in reduction process.

2.3. Proposed mechanism

It is evident that reduction kinetics of N-nitrosamines is very similar in some aspects to cupferron reduction. So it is may be supposed that the first stage of Kolthoff and Liberti scheme (4) is correct. But it should be stated that the intermediate resulted from this two-electron process does not look as stable one. Presumably, it undergoes transformation into phenyldiazonium cation:



Electroreduction of aryldiazonium cations is a complex process, usually it has two stages with the first one reversible [23-26]. Preparative electrolysis at the potential of the first process produces arylmercury salts; at the potential of the second one N-aryl hydrazine is formed. In acidic solutions the mechanism of this process may be represented by the scheme [25]:



Side reactions are promoted by stirring of the solution and high temperature. The final product is substituted hydrazine, and this makes phenyldiazonium cation quite acceptable intermediate in NPHA reduction.

In alkaline media aryldiazonium cation transfers into diazotate anion. It is generally supposed that diazotates are not electroactive, and their reduction on mercury electrode is achieved indirectly, by sodium amalgam formed [27]. But it is known that phenyldiazotate can be reduced up to pH 11.5, presumably due to shift to diazohydroxide by protonation [26]. The mechanism of the reaction is not known; it is likely that we could have here another kinetically hindered process. Unfortunately, little attention has been paid to electrochemistry of diazotates. Using tetraalkylammonium salts as supporting electrolyte instead of sodium

ones, for instance, could be more useful in making decision about their electrochemical activity or inactivity.

The mechanism proposed is only speculative; there is no direct evidence of phenyldiazonium formation during cupferron reduction. But Aleskovskii et al. have found well formed peaks on a.c. polarogram of cupferron at pH 1-3 [8], and this fact is difficult to expect for a process with such an evident irreversibility, otherwise it has some reversibly reducing intermediate. Unfortunately, a.c. polarographic data on cupferron reduction are very limited. Diazonium cation is one of the most possible intermediate species, but the published data for its reduction in alkaline solutions are very scarce and could not be helpful in elucidating the reaction mechanism. Anyway, there is no other potential intermediate that is really stable and has some reversible reduction stages.

3. CONCLUSION

The data observed reveals that it is difficult to assign a starting point of cupferron reduction to some of its particular electroactive groups. N-nitroso group looks like the best candidate, but kinetic parameters of aromatic nitrosamine reduction differ drastically from ones of cupferron. It may be a result of completely different reduction mechanism. Formation of stable intermediate, aryldiazonium cation, in the case of cupferron electroreduction can explain some peculiarities of this process.

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