

Electrochemistry and Spectroscopy of an Energetic Material FOX-7. A Molecular Approach to Degradation Mechanism

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Abstract – Recently synthesized a new energetic material 2,2-dinitroethene-1,1-diamine (FOX-7) has significant potential for application due to its high performance and very low sensitivity. Generally, explosion is based on thermally initiated chain of intramolecular redox reactions. It has been found that electrochemical reduction of FOX-7 in aqueous as well as in non-aqueous solutions is also able to provoke the chain of follow-up processes leading to total decomposition of the parent substance. As intermediates radical species were proved in aprotic media. Moreover, instead of organic amines, namely gaseous products were identified after exhaustive electrochemical reduction. For these investigations various electrochemical methods both in analytical, as well as in preparative scale were utilized, together with UV-Vis spectroscopy. The detailed understanding of the mechanism and analysis of individual reaction steps is under further study. **Copyright © 2012 Praise Worthy Prize S.r.l. - All rights reserved.**

Keywords: 2,2-Dinitroethene-1,1-Diamine, Degradation Mechanism, Electrochemistry, FOX-7, Spectroscopy

I. Introduction

Recently synthesized 2,2-dinitroethene-1,1-diamine (Fig. 1) is a new energetic material known under the name FOX-7 [1]. The energetic materials are generally divided to the three categories: propellants, fuels and explosives. FOX-7 is classified as an explosive material.

As explosives are often used: 1) various types of nitrites (for example NH_4NO_3); 2) organic azides particularly those with a double bond $\text{C}=\text{C}$ and more than one azido group (1, 4-diazidobut-2-en); 3) salts of nitrogen oxide and 4) substances which contain a nitro group in its structure bound to a carbon, oxygen or nitrogen atom.

The well known nitro compounds used as explosives are NG (1,2,3-nitroglycerine), TNT (2,4,6-trinitrotoluene), RDX (1,3,5-trinitro-1,3,5-triazacyklohexan) and picric acid. To compare the power and destructive effects of explosives, physically measurable parameters like detonation velocity and pressure, the volume of gaseous products, heat of explosion etc. were determined and/or calculated.

Some of these properties of FOX-7 are shown in Table I in comparison with some other well known explosive materials. The main advantage of FOX-7 is its very low sensitivity whereas its high performance is retained. The structure of FOX-7 due to the presence of amine groups, enables a.o. formation of inter- and intramolecular hydrogen bridges. Their presence makes the compound very stable and thermally resistant (decomposition above 200°C) and most probably, this is also the reason for reduced impact and friction sensitivity of FOX-7.

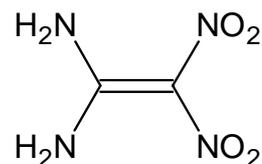


Fig. 1. 2,2-dinitroethene-1,1-diamine (FOX-7)

Simultaneously, this structural feature can have an influence on the mechanism of degradation (explosion). This is the reason for an extended study of electrochemical reduction of the title compound.

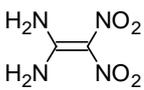
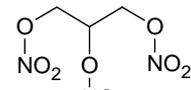
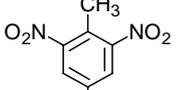
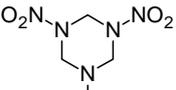
The mechanism of the process during explosion of nitro-explosives is not known in detail. Some authors [2], [3], based on experiments, calculation and molecular simulations support the idea that the bonds $\text{C}-\text{NO}_2$, $\text{N}-\text{NO}_2$ and $\text{O}-\text{NO}_2$ are the most prone to be split and thus probably represent a detonation trigger.

The molecule of FOX-7 is, however, interesting not only as a material with significant potential for application, but also for fundamental research of intramolecular interactions and electron transfer reactions in order to understand the reaction abilities of such complicated electron system with multiple redox centers.

One part of this molecule bears two geminal easily reducible nitro groups and the opposite part is represented by two electron-donating amino groups.

The difference between the oxidation state of amino groups (-III) and nitro groups (+III) represents six electrons.

TABLE I
 COMPARISON OF PROPERTIES OF FOX-7 WITH SOME OTHER EXPLOSIVES

Properties	 FOX-7 [4]	 NG [6]	 TNT [6]	 RDX [6]
Density [g/cm ³]	1.880	1.591	1.654	1.82
Molecular weight	148.079	227.1	227.1	222.1
Oxygen balance [%]	-21.6	+3.5	-73.9	-21.6
Impact sensitivity [J]	> 30	0.2	15	7.5
Friction sensitivity [N]	> 350	353	353	120
Detonation velocity [m/s]	8870	7600	6900	8750
Detonation pressure [GPa]	33.96	24.7446 [7]	21.972 [7]	34.63
Volume of gaseous products [cm ³ /g]	900 [5]	716	825	903

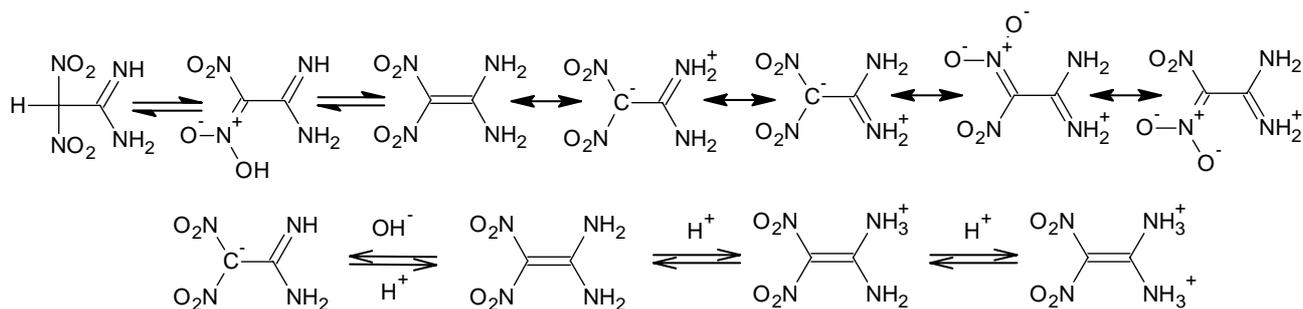


Fig. 2. Mesomeric, tautomeric and acidbasic equilibria of FOX-7

This combination creates a so called push-pull effect of electrons. Therefore the electron distribution is unbalanced enabling intramolecular electron transfer reactions. FOX-7 can be seen as a resonance hybrid of several mesomers and tautomers being in complicated equilibrium (Fig. 2). This fact is consistent with the relative stability of FOX-7.

In the last decade, many papers concerning synthesis, chemical, thermochemical and other physicochemical properties of FOX-7 have appeared and have been recently reviewed [8]. However, its redox properties have not been yet studied electrochemically. Electrochemistry is unique and often irreplaceable method for investigation of redox reaction mechanisms of organic and coordination compounds, including the respective equilibria.

However, this approach was only rarely used for fundamental studies of explosives although the polynitro compounds are generally attractive for electrochemists. In past only few papers have appeared in this field. For example in paper [9] polarographic methods were used for analysis of small samples of explosive mixture of TNT with RDX, HMX (1,3,5,7-tetranitro-1,3,5,7-tetraazacyklooctane) and DNT (2,6-dinitrotoluene).

Nowadays an electrochemical approach in this field is used mainly for developing of sensors for detection of explosives. There are same examples of sensors for detection of TNT: electrochemical sensors based on cyclic voltammetry [10] and another sensor based on graphene [11].

The graphene-based electrochemical sensing platform for sensitive determination of explosive nitro-aromatic compounds is also used in another work [12]. Besides that in paper [13] an electrochemical oxidation at boron-doped diamond electrodes was examined as a possible technique for the remediation of water contaminated with nitramine explosives.

Generally, explosion is a thermally initiated chain of fast intra- (and/or inter-) molecular redox reactions, which are very exothermic and generate high amount of gaseous products. The presence of two geminal reducible nitro groups in neighborhood of two geminal oxidizable amino groups in the molecule of FOX-7 gives a chance to initiate its degradation electrochemically.

The preliminary results qualitatively supported this idea [14].

The aim of this contribution is to use a rather complex electrochemical approach for investigation of reduction (eventually oxidation) abilities of FOX-7 in aqueous as well as in aprotic media for deeper insight into its degradation mechanism. For this purpose UV-Vis spectroscopy was used along the electrochemical experiments to characterize corresponding intermediates.

II. Experimental

The yellow crystalline 2,2-dinitroethene-1,1-diamine (FOX-7) was received directly from the laboratory of organic synthesis at the University of Pardubice. It can be easily dissolved in dimethylformamide (DMF), dimethylsulfoxide (DMSO), in cyclic lactones like *N*-

methyl pyrrolidone (NMP) and also in diluted hydrochloric acid. On the other hand, in water and in alcohols, acetone or chlorinated solvents is very poorly soluble. Therefore for analytical experiments in aqueous solutions a stock solution of 0.01 M FOX-7 in DMF was every day freshly prepared and the adequate volume was transferred by a Hamilton microsyringe into electrochemical cell filled with a deoxygenated 0.1 M aqueous buffer yielding 3.2×10^{-4} , 6×10^{-4} and 9.6×10^{-4} M solutions of FOX-7, respectively. For exhaustive electrolyses and coulometry the concentration of FOX was higher at least by one order of magnitude.

The investigation proceeded both in aqueous buffered solutions as well as in aprotic media. The following buffers were utilized: phosphate for pH 2–3, 5–8 and 10–11, acetate for pH 4–5 and borate for pH 8–10. For preparation of all investigated solutions the standard chemicals for buffers of p.a. grade were used as received. For the acidic solutions sulfuric acid of various concentrations (0.05 to 5 M) was used, for the very basic media solutions of sodium hydroxide was utilized. Dimethylformamide (DMF) and acetonitrile (AN) with tetrabutylammoniumtetrafluoroborate (TBATFB) or tetrabutylammoniumhexafluoro-phosphate (TBAHFP) as electrolytes were used as aprotic media.

For all analytic and electrolytic experiments a three-electrode system was used. Classical dropping mercury electrode (DME) with a controlled drop time (2 s) was utilized in DC-polarography. Hanging mercury drop electrode (HMDE) was used for cyclic voltammetry and mercury pool electrode (area cca. 1 cm^2) was used for electrolysis. The mercury pool was stirred during electrolyses by a magnetic bar. A platinum wire or platinum foil served as an auxiliary electrode and the potentials were controlled against saturated calomel reference electrode (SCE).

Polarographic and voltammetric experiments were carried out in an undivided 10 ml cell with reference electrode separated by a salt bridge. The electrolyses proceeded in a divided H-type cell, where anodic and cathodic parts are separated by a dense frit.

The experiments were conducted by the analog potentiostat PA3 or PA4, both Laboratorní přístroje Praha with an XY recorder or by a digital potentiostat PGSTAT30, Autolab. The scan rate 5 mV/s was used for polarography and scan rate 50–500 mV/s for cyclic voltammetry. The pH was checked by pH/ORP Meter Hanna Instruments HI 3220. The solution was deaerated by argon for the electrochemical experiments.

An analysis of gaseous products during electrolysis in 0.5 M H_2SO_4 was realized by on-line connected gas

chromatograph (GC Hewlett Packard 6890). The GC analysis was simultaneously supplemented by mass spectroscopy analysis using an on-line connected quadrupole mass spectrometer (Pfeiffer OmniStar, GSD 301 C). The electrolysis run in galvanostatic mode (current 10 mA).

The stream of He was 15 ml/min. Every analysis takes 15 minutes. One gaseous sample from electrolytic cell was injected in the branch with a thermal conductivity detector (TCD) and second gaseous sample in the second branch with a flame ionization detector (FID) for analysis of organic products. More details about experimental set-up are in article [14].

Spectrometric measurements were carried out by UV-VIS spectrophotometer Shimadzu UV1800.

III. Results

The electron rich amino groups are expected to be electrochemically oxidizable. However, all attempts to oxidize FOX-7 under various conditions in aqueous as well as in aprotic media (even in liquid SO_2) were unsuccessful.

Therefore the main attention is devoted to electrochemical reduction.

III.1. Electrochemical Reduction in Aqueous Buffers

III.1.1. Electrochemical Studies in Analytical Scale

The electron poor nitro compounds are generally easily reducible. According to the expectation, electrochemical reduction of FOX-7 proceeds smoothly and in several steps. On the polarogram, from four to six reduction steps (polarographic waves) were found at each pH value, all irreversible (proved by cyclic voltammetry).

Within the whole pH range, together eight processes (R1–R8) were identified. Four of them are present in all pH, the others appeared only in some pH ranges [14].

The sum of polarographic limiting currents present at any pH always corresponds to about 18 transferred electrons per one molecule of starting FOX-7, as estimated using the comparison with several nitro standards like *p*-nitrotoluene, *p*-dininitrobenzene or *p*-nitroanisole.

During experiments a change of colors in various pH was observed. Using UV-Vis spectroscopy we found that FOX-7 is presented in three different forms in aqueous solutions in dependence on pH (Fig. 4). All transitions between these acidobasic forms are reversible.

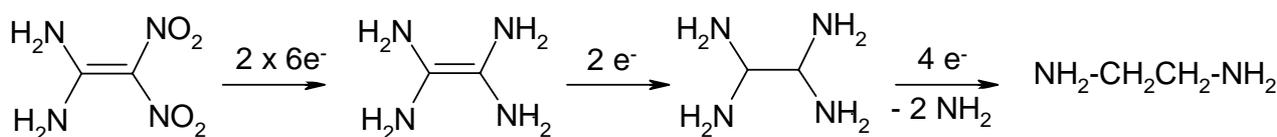


Fig. 3. Overview of expected possible reduction reactions of FOX-7

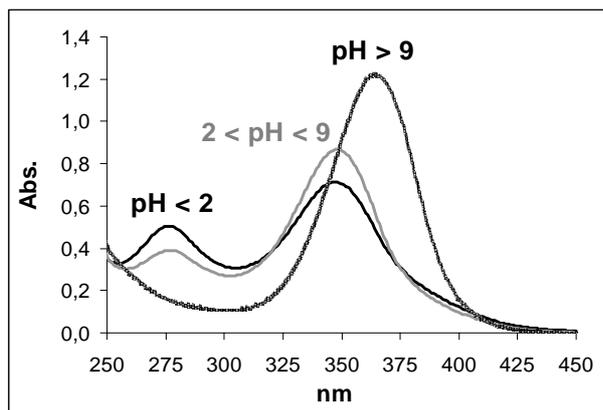


Fig. 4. The UV spectra of FOX-7 in aqueous buffered solutions. Concentration of FOX-7 is 8×10^{-5} mol/l

For the structure identification of the respective form, ^{13}C NMR analysis was used. Because of poor solubility of FOX-7 in neutral water solution, only the anionic structure in basic pH could be confirmed (Fig. 5). Nevertheless, this enabled us to estimate the other two forms.

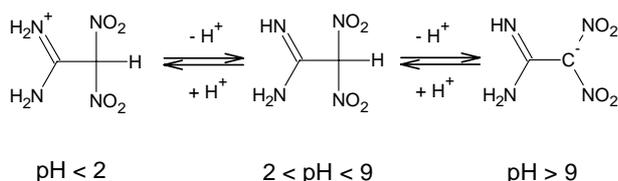


Fig. 5. Structures of FOX-7 in aqueous buffered solutions

III.1.2. Electrochemical Studies in Preparative Scale

The preparative electrolyses were carried out in 5 M, 0.5 M and 0.1 M sulfuric acid at four potentials: -0.25 V, -0.4 V, -0.8 V and -1.05 V. The charge passed during the exhaustive potentiostatic electrolytic reduction of FOX-7 in acidic buffered media, however, corresponds to the consumption between 4–6 electrons per molecule only, which is much less than under polarographic conditions. After exhaustive electrolysis the expected product ethan-1,2-diamine was, however, never found.

The course of the electrolysis was followed polarographically.

During whole electrolysis a new cathodic wave at -0.95 V linearly increased with passed charge. It was proved by classical qualitative analytical procedure (using Griess-Lung reagent) [15] and also polarographically by adding an authentic sample in the solution, that this product is a nitrite anion. In the next electrolytic experiments, argon after passing through the solution was collected and by using Nessler test NH_4^+ ions were detected.

The solutions after preparative electrolysis were analyzed for the organic amines, the dried residue was always extracted and the extract was checked by thin-layer chromatography (TLC).

However, neither UV detection, nor application of iodine vapors and also direct NMR or MS analyses did reveal any individual organic product.

Therefore our attention was turned to eventual gaseous products. For analysis of gases, an “on-line” connected gas chromatograph and mass spectrometer were employed. Table II shows the evolution of N_2 , NO and N_2O during electrolysis of FOX-7. Any other gases, neither volatile hydrocarbons nor carbon oxides, were observed under these conditions.

III.2. Electrochemical Reduction in Aprotic Solvents

III.2.1. Electrochemical Studies in Analytical Scale

The polarographic study of FOX-7 in aprotic solvent (AN resp. DMF) was performed in a series of concentrations of FOX-7: 0.4×10^{-4} , 1×10^{-4} , 2×10^{-4} , 3×10^{-4} , 5×10^{-4} , 6×10^{-4} , 7×10^{-4} and 8×10^{-4} mol/l. Using a 2 s controlled drop-time, three reduction steps were observed (Fig. 6). The cyclic voltammetry on mercury drop revealed that only the most negative reduction step is reversible.

TABLE II
TABLE OF GASEOUS PRODUCTS OBSERVED BY THE ON-LINE SYSTEM EC-GC-MS DURING THE ELECTROLYSIS IN $0.5\text{M H}_2\text{SO}_4$ IN GALVANOSTATIC MODE, EXCESS OF FOX-7. CONCENTRATIONS OF GASES ARE IN PPM
(THE COLORED ZONE REPRESENTS THE COURSE OF ELECTROLYSIS)

Analysis	O_2	N_2	NO	N_2O	
1	426.4	1368.7			
2	406.8	1354.3			
3	417.8	1340.6			
4	443.5	1446.2			
The start	5	425.5	1372.5		
6	408.6	1543.6	151.5	210.2	
7	416.8	1640.0	552.3	234.8	
8	423.9	1677.5	773.8	283.7	
9	418.6	1662.4	916.9	288.3	
10	406.9	1666.4	1304.6	301.1	
11	425.0	1813.5	1271.5	294.9	
12	408.6	1696.6	1335.4	312.8	
The end	13	422.8	1743.3	972.3	316.9
14	411.1	1388.9		34.7	
15	415.4	1361.1		15.6	

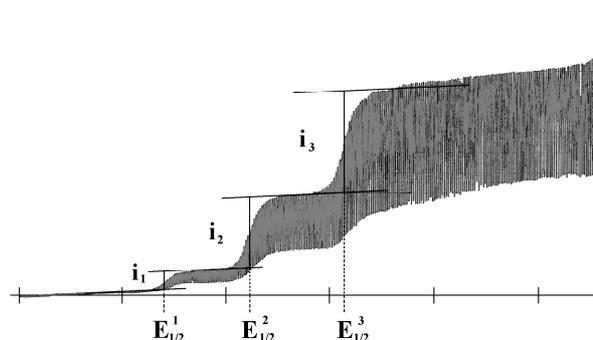


Fig. 6. The typical polarographic curve of FOX-7 in AN on mercury electrode. Concentration of FOX-7 6×10^{-4} mol/l

The limiting current of the first reduction wave (around -0.6V) linearly increased until the concentration of 1×10^{-4} mol/l in AN was reached. At higher concentration this wave remained unchanged, whereas a second wave appeared at the potential around -1.1 V.

The sum of limiting currents of the two first polarographic waves continues to be linearly dependent on concentration of FOX-7. The small first wave represents electrochemical reduction of FOX-7 on a "clean" electrode when the product is strongly adsorbed on electrode surface. This fact makes the reduction easier and a shift to less negative potentials is observed (so called adsorption pre-wave). After saturation of the electrode surface this effect is not more operating and the regular diffusion-controlled reduction occurs (second wave). The third, reversible reduction process is also diffusion controlled.

The sum of limiting currents of all three polarographic waves corresponds to consumption of two electrons, as estimated by comparison with nitro- standards like *p*-nitrotoluene, *p*-dinitrobenzene and *p*-nitroanisole. The first electron is consumed in the first two reduction steps; the third wave corresponds to the second electron.

Generally, in aprotic solvents (AN and even more in DMF) the intermediates with anion character are stabilized due to the absence of protons. Even here the question of the structure which is really reduced is important. For this purpose a series of solutions of FOX-7 were prepared starting with dry AN to which was then gradually added a defined amount of water. These solutions were investigated by DC-polarography and by UV-Vis spectroscopy. The polarographic results show that there is no big influence of small amount of moisture on reduction process. But addition of more water moves reduction potentials to the more positive values and makes the reduction process multielectron.

UV-Vis spectra of the above mentioned series of solutions show that FOX-7 is present in different form in aprotic and in aqueous solutions (Fig. 7). Its structure in dry aprotic solvent was confirmed by ^{13}C NMR analysis and corresponds to the original structure which is presented in literature (Fig. 1).

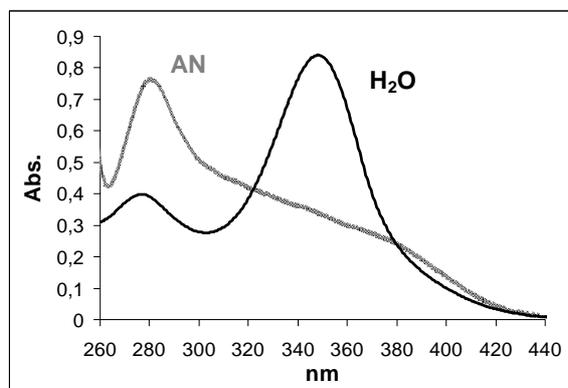


Fig. 7. The UV spectra of FOX-7 in dry AN and in water
Concentration of FOX-7 is 8×10^{-5} mol/l

III.2.2. Electrochemical Studies in Preparative Scale

The exhaustive reductive electrolysis of FOX-7 was performed in AN, resp. DMF. The consumption of electrons is dependent on applied potential and fully corresponds to the polarographic results: during electrolysis at potential -1.3 V (on the limiting current of the second reduction step) the value of consumed electrons is approximately one per molecule. The second consumed electron passes during electrolysis at the last reduction step (at -1.8 V).

On the *i-t* curve recorded during electrolysis in AN at -1.8 V (Fig. 8) it is evident the change of mechanism after passing of the first electron per molecule, whereas the consumption of the second electron follows the theoretical (exponential) pattern.

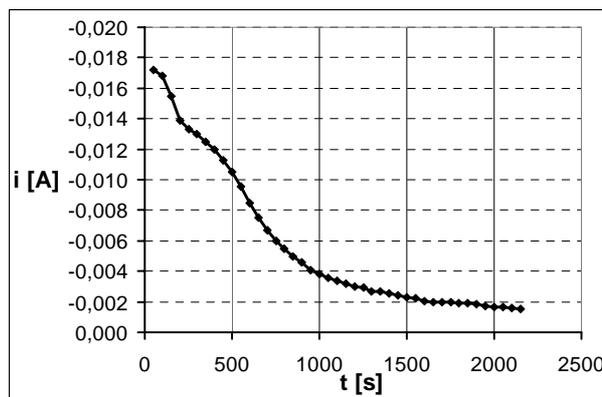


Fig. 8. The chart of dependence of current on time during electrolysis of FOX-7 in AN + 0.1M TBATFB in potential -1.8 V. W...Hg pool, Aux...Pt wire, Ref...SCE, concentration of FOX-7 7×10^{-3} M

During electrolysis in aprotic solvents (in AN as well as in DMF) the solution changes its color (Fig. 9). Before electrolysis the solution is light yellow. Upon turning on the electrolysis, the color of solution immediately starts to change into orange. When the electrolysis proceeds at the potential of the limiting current of the wave i_2 , the solution remains deep orange.

At the potential of -1.8 V after passing approx. one electron per molecule the solution becomes gradually more and more green. This color is not stable and belongs to radical intermediate(s) which are formed during the last reduction step. After re-oxidation its color is (reversibly) changed back to orange.

During the electrolysis, UV-Vis spectra were continuously recorded in order to follow quantitatively the color changes (Fig. 10). The spectra show an increase of absorbance in UV as well as in visible region. The interpretation of the spectra suggests formation of two different stable products during the first irreversible reduction at potential -1.3 V, which manifest themselves by peaks at 215 and 365 nm, whereas the band at 280 nm (FOX-7) is disappearing. Upon the reduction at -1.8 V new bands at 306 and 710 nm increase at the expense of the primary spectrum. The latter increasing bands belong to the reversibly formed radical(s).



Fig. 9. Changes of colors during electrolysis in AN + 0.1M TBATFB in potential -1.8 V

This observation is in agreement with the electrochemical data and the preliminary EPR-spectroelectrochemical results confirm the presence of a stable radical during the second reduction process at the most negative potentials.

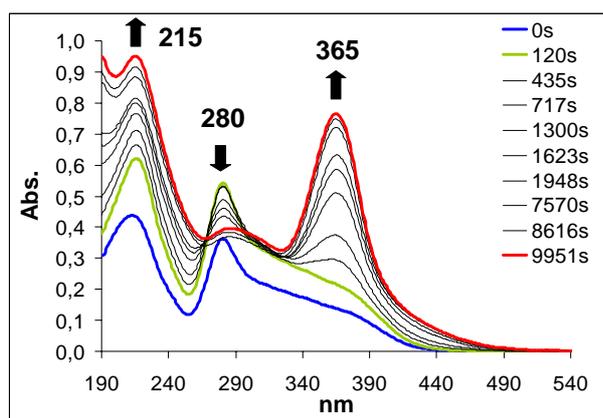


Fig. 10. Evolution of UV-Vis spectra during electrolysis of FOX-7 in AN + 0.1M TBATFB at potential -1.3 V. Concentration of FOX-7 during electrolysis 0.0125 mol/l. Concentration of FOX-7 in UV-Vis measurements 8×10^{-5} M

The products of exhaustive electrolysis were analyzed by extraction, thin layer chromatography and direct NMR analysis. Neither the expected ethan-1,2-diamine, nor another organic amine was identified in the residue after electrolysis. Thin layer chromatography only revealed the presence of a mixture of several products, their separation, isolation and identification was up to now unsuccessful. The attempts to separate the products by preparative liquid chromatography and to identify them using mass spectrometry is still running.

IV. Discussion

The main goal of this work is the discrepancy between the expected and the observed number of consumed electrons during electrochemical reduction of the title compound. Considering the structure, the molecule of FOX-7 is bearing two nitro groups, one double bond and primary amine groups. In aqueous media [14], this molecule could be theoretically reduced by 18 electrons to the final product ethan-1,2-diamine (Fig. 3). In aprotic media the reduction proceeds more negatively (due to the absence of protonation reactions). In AN or DMF, reduction of one nitro-group should involve 4 electrons giving rise a hydroxylamino derivative. Therefore consumption up to 8 electrons should be expected in the

available potential region.

The experimentally obtained sum of polarographic limiting currents in aqueous solutions really corresponds to 18 electrons, in agreement with expectations. The number of consecutive reduction waves and their changes with pH [14] points to the fact that in various pH regions different molecule is preferentially reduced and thus different mechanism is involved. On the other hand, during exhaustive electrolyses, only 4–6 electrons were consumed, though all starting FOX-7 was decomposed. Similarly in aprotic solvents the electron consumption during electrochemical experiments is much lower than the expectations.

The interpretation of this discrepancy is following.

The degradation of FOX-7 is initiated electrochemically, but it continues prevalently by follow-up intra- or intermolecular redox reactions. These chemical processes are relatively slow and of higher order, therefore they become evident and operating during long-term electrolyses at high concentration of the substrate, whereas on the dropping mercury electrode the available time scale is too short (2 s). This explains the difference in observed electron consumption.

The fundamental mechanistic question is: What is really electrochemically reduced in the first, electrochemical step: nitro or tautomeric imino group (cf. Fig. 2)? In addition to this, due to the presence of two amino groups, one could expect in aqueous solutions at least two protonation/deprotonation equilibria and thus three forms of FOX-7: basic, mono- and diprotonated with their pKa values. As mentioned above, FOX-7 is a very stable molecule and the conjugation of free electron pair of one amino group with the nitro group surely contributes to its stability.

Therefore we have to consider both acidobasic and tautomeric equilibria between enamine and imine form. The latter structure involves a very acid hydrogen atom attached to the sp^3 carbon atom which could be split of in aprotic or basic media giving raise another acidobasic system (cf Fig. 2).

Based on the spectrometric results, in aqueous solutions the imino form is preferentially reduced. In dry aprotic solvent, however, the original dinitro diamino structure was proved by NMR.

This finding is consistent with the polarographic results in aprotic solvent, where the first step was attributed to a reduction of nitro group complicated by autoprotonation mechanism [16], since the first wave is irreversible (theoretically involving 4/5 electron) and the second one reversible at more negative potentials.

The UV-Vis spectra recorded during exhaustive electrolysis in aprotic solvent show an increase of absorbance in UV as well as in visible region. Their interpretation suggests formation of two different stable products during the first irreversible reduction at potential -1.3 V. Upon the electrolytic reduction of FOX-7 at higher negative potential new bands on UV-Vis spectra increase. These bands belong to the reversibly formed radical(s).

The most exciting result is the proved presence of gaseous products during electrolysis (cf. Table II). Together with the surprisingly low consumption of electrons it suggests a hypothesis, that the above studied degradation is analogous to the process during explosion.

V. Conclusion

The redox properties of the novel energetic material FOX-7 (2,2-dinitroethene-1,1-diamine) were investigated electrochemically in aqueous buffers as well as in aprotic media (AN, DMF). Three fundamental questions for studies of the overall mechanism were solved: a) the total number of consumed electrons both in aqueous and aprotic solution; b) the structural form of FOX-7, which is really reduced under the given conditions; c) presence of radical intermediates, their stability and reversibility of formation.

The high number of follow-up reactions, significant difference between expected and found consumption of electrons during preparative electrolyses under all conditions and generation of gaseous products can be explained by the electrochemically initiated total degradation of the explosive FOX-7, where a chain of intramolecular follow-up redox reactions takes place which could be analogous to the explosion process. The detailed reaction pathway is under further study.

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