

Electrochemical investigation of 2,2-dinitroethene-1,1-diamine (FOX-7) in aqueous media

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Abstract Redox properties of 2,2-dinitroethene-1,1-diamine (FOX-7) were electrochemically investigated by DC polarography, cyclic voltammetry and preparative electrolyses, and electroreduction products were analysed. The polarographic reduction of FOX-7 in aqueous buffered solutions exhibited a total sum of limiting currents corresponding to the expected 18 electrons. This result fits well with the chemical reduction of this energetic material resulting in ethan-1,2-diamine. Exhaustive electrolysis, however, did not yield this product and the passed charge for total degradation of this compound corresponds only to 4–7 F. As the main products, gaseous N_2 , N_2O , NO and NH_3 were proved by combination EC–GC–MS and, besides that, nitrite anions and ammonia ions were identified by other methods. All these observations suggest that instead of electrochemical reduction, an electrochemically initiated degradation process accompanying the exhaustive electrolysis occurs. This seems to be analogous to the chain of reactions during explosion, which are slowed down by a very low concentration and cooled by the solvent.

Keywords 2, 2-Dinitroethene-1, 1-diamine · FOX-7 · Reduction · Polarography · Electrolysis · Degradation mechanism

Introduction

2,2-Dinitroethene-1,1-diamine, $(H_2N)_2C=C(NO_2)_2$ (FOX-7) is a recently designed, developed [1–6] and broadly tested energetic material with a significant potential for application due to its high detonation energy and velocity (about 5,000 J/g and 8,800 m/s, respectively [7]) and simultaneously low impact and friction sensitivity and high temperature of ignition (over 220 °C [8]). In the last decade, many papers appeared about its synthesis, chemical, thermochemical and other physicochemical properties (they have been recently reviewed [9]); however, its redox properties, namely, an electrochemical study, is still missing.

Besides of the abovementioned applicability, this molecule is one of the most interesting molecules with multiple redox centres. The structure is remarkable due to the combination of two geminal, easily reducible nitro groups in the neighbourhood of two strongly electron-donating amino groups. This combination represents a typical case of “push–pull” system also allowing intramolecular electron transfer. Due to this fact, the electrochemical approach is of highest interest since it can give some insight in the mechanism of chemical transformations of this uncommon compound. Taking into account the molecular structure, functional groups most probably will not retain their original redox properties since several redox centres are very close to each other and their mutual intramolecular as well as intermolecular interactions should be expected. Due to this fact, the formation of various conjugated intermediate systems with specific electronic qualities should be considered.

Our preliminary experiments in aqueous solutions as well as in liquid SO_2 reveal that the electrochemical oxidation of FOX-7 does not occur in the accessible potential range. Therefore, we oriented our efforts only to electrochemical reduction. The presented contribution deals

This article is dedicated to the 70th birthday of Fritz Pragst.

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with a fundamental electrochemical study in buffered aqueous solutions using standard electrochemical methods, both steady state and dynamic, in an analytical as well as preparative scale. Besides that, on-line EC–GC–MS experiments were used for identification of products.

Experimental

Chemicals

The sample of FOX 7 was received directly from the laboratory of organic synthesis at the University of Pardubice. Due to the low solubility of FOX-7 in water, a 0.01-M stock solution in dimethylformamide was freshly prepared everyday and the adequate volume was transferred by a Hamilton microsyringe into a electrochemical cell filled with deoxygenated buffer according to the need. For the acidic solutions, sulfuric acid of various concentrations was used (0.05 to 5 M); for the very basic media solutions, sodium hydroxide was utilized. For the other pH values, 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 the preparation of all investigated solutions, the standard chemicals for buffers of p.a.-grade were used as received. The concentration of FOX-7 in analytical experiments was changed between 0.08 to 0.96 mM; the concentration for exhaustive electrolyses was mostly 0.01 M or 0.03 M, eventually 0.07 M.

Experimental setup

For all electrochemical experiments, a three-electrode system was used: as the working electrode served dropping mercury electrode, hanging mercury drop electrode (HMDE) or mercury pool; for comparison, platinum stationary electrode was also used. As auxiliary electrode, a platinum wire or platinum foil was used. The potentials were controlled against saturated calomel reference electrode. Polarographic and voltammetric experiments were carried out in an undivided 10-ml cell with the reference electrode separated by a salt bridge. 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 by Laboratorní přístroje Praha with an XY recorder or by a digital potentiostat PGSTAT30, Autolab. The controlled drop time was 2 s; scan rate was 5 mV/s for polarography and 20–200 mV/s for cyclic voltammetry. The mercury pool was stirred during electrolyses by a magnetic bar. The pH was checked by pH/ORP Meter Hanna Instruments HI 3220. The solution was deaerated by argon for the electrochemical experiments.

On-line connected gas chromatograph (GC Hewlett Packard 6890) was employed for the analysis of volatile products formed during the electrochemical experiments. The stream of helium (20 ml min^{-1}) was used for degassing of electrolyte and transport of the formed products for analysis. The connections between the electrochemical cell and the gas chromatograph were heated to avoid any condensation. Two gaseous samples were simultaneously injected with ten-port valves for analysis. In the branch with a thermal conductivity detector (TCD), a Hysep column (packed column) was used for the retention and removal of organic compounds and water; columns of HP-Plot Q ($30 \text{ m} \times 0.53 \text{ mm} \times 40 \text{ } \mu\text{m}$ film thickness) and a Molecular sieve 5A ($30 \text{ m} \times 0.53 \text{ mm} \times 25 \text{ } \mu\text{m}$ film thickness) were used for the separation of N_2 , O_2 , CO, CO_2 and N_2O . HP-Plot Q separated CO_2 and N_2O from N_2 , O_2 and CO. The sixth port valve was used to bypass the column Molecular sieve 5A during the analysis of CO_2 and N_2O on TCD. After the analysis of CO_2 and N_2O , the mixture containing N_2 , O_2 and CO was separated with the column molecular sieve 5A and monitored on the TCD. The following conditions of analysis were used: carrier gas He, pressure 20 psi, splitless mode, loop volume 1 ml, by-pass of molecular sieve 5 A at 5.1–10.0 min, constant temperature $40 \text{ }^\circ\text{C}$ for 23 min, then temperature gradient $20 \text{ }^\circ\text{C min}^{-1}$ to $200 \text{ }^\circ\text{C}$. In the second branch, a HP-Plot Q column ($30 \text{ m} \times 0.53 \text{ mm} \times 40 \text{ } \mu\text{m}$ film thickness, carrier gas He 7.9 ml min^{-1} , constant flow mode, split ratio 1:50, loop 250 μl , constant temperature $40 \text{ }^\circ\text{C}$ for 23 min, then temperature gradient $20 \text{ }^\circ\text{C min}^{-1}$ to $200 \text{ }^\circ\text{C}$) and a flame ionization detector were used for the analysis of organic products. The analysis of gaseous products was supplemented by mass spectroscopy analysis carried out simultaneously with the GC analysis using an on-line-connected quadrupole mass spectrometer (Pfeiffer OmniStar, GSD 301 C).

Results and discussion

DC polarography

When starting to investigate a new electrochemically “unknown” compound, an application of dc polarography is very advantageous particularly for primary reduction study. The reasons are namely: (a) sensitivity and reproducibility of this technique, (b) a complex information from the polarogram as well as from the shape of individual oscillations about the nature of individual processes involved (faradaic or non-faradaic, diffusion, kinetic or catalytic control, adsorption and desorption, etc.), (c) direct estimation of the number of transferred electrons and, finally, (d) the broadest cathodic potential window.

The polarographic study was performed with 1.6×10^{-4} , 3.2×10^{-4} and 9.6×10^{-4} M solutions of FOX-7 in

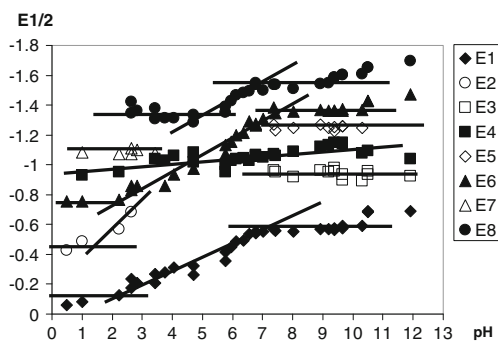


Fig. 1 Plot of the dependences of $E_{1/2}$ vs. pH of all (E1–E8) observed reduction waves (concentration of FOX-7 1.6×10^{-4} mol/l)

0.1-M aqueous buffers over the whole range of pH. The linear dependence of main observed limiting currents on concentration as well as on the square root of the mercury column height points to their diffusion control. In small waves, the evaluation of the i vs. concentration plot is uncertain. All prepared solutions in the cell were stable for at least within 1 h.

Using a 2-s controlled drop-time, four to six reduction steps (polarographic waves) were found at each pH value—all irreversible (proved by cyclic voltammetry). Within the whole pH range, eight processes (E1–E8, cf. Fig. 1) were together identified. Their appearance (presence), shifts of reduction potentials and development of limiting currents depend on the pH value (Figs. 1, 2 and 3).

In all graphs depicted in Fig. 1, the reduction potentials in acidic solutions (pH 0–2) are independent on pH. This is the region, where prevalently protonated

forms are present in the solution and reduced (2). In the pH region 2–7, the non-protonated species prevail in the bulk of the solution. The shift of the reduction potentials suggests that reduction at an electrode (2) is preceded by a protonation step (1) and the potential is thus affected by pre-protonation equilibria depending on pH. (The respective slopes are presented in Table 1.) Hence, the pH value of the intersection of the first two straight lines corresponds to the pK_a of the compound X [10] (generally precursors or intermediates). In basic solutions at $pH > 7$, the independence of the reduction potential on pH is caused by the absence of a proton transfer in the process (3):



The differences in the slopes $dE_{1/2}$ vs. dpH point to the fact that the reduced species are protonated by one or even by two protons (probably in E2) and that the protonation occurs not always directly at the reducible centre but also in other parts of the molecule more distant from the reduction centre.

From the high number of observed reduction processes and from the different slopes, it is evident that the reduction of FOX-7 is a very complicated electrochemical system involving at least eight electroactive intermediates generated in chemical precedent, parallel as well as follow-up

Fig. 2 Plot of the dependences of i vs. pH: **a**=E1, **b**=E2, **c**=E3, **d**=E4 (concentration of FOX-7 3.2×10^{-4} mol/l)

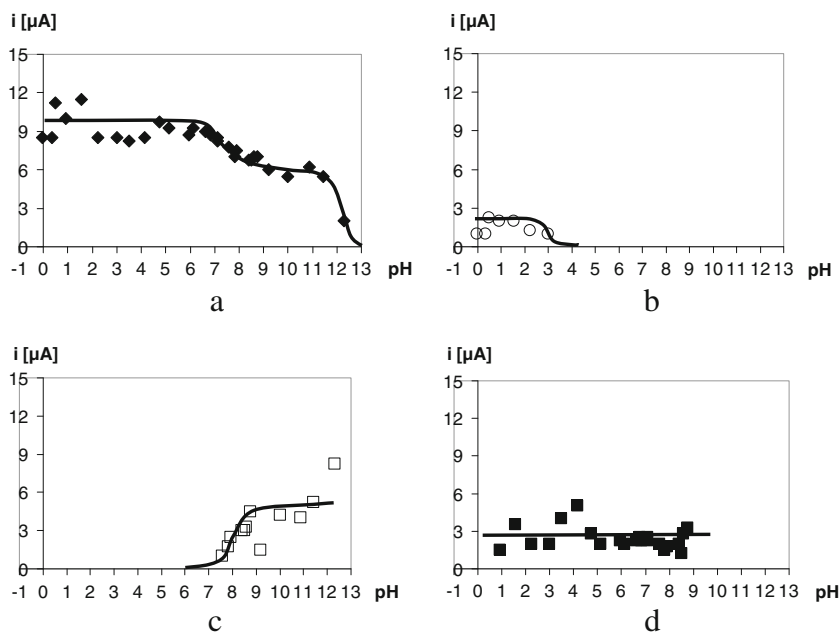
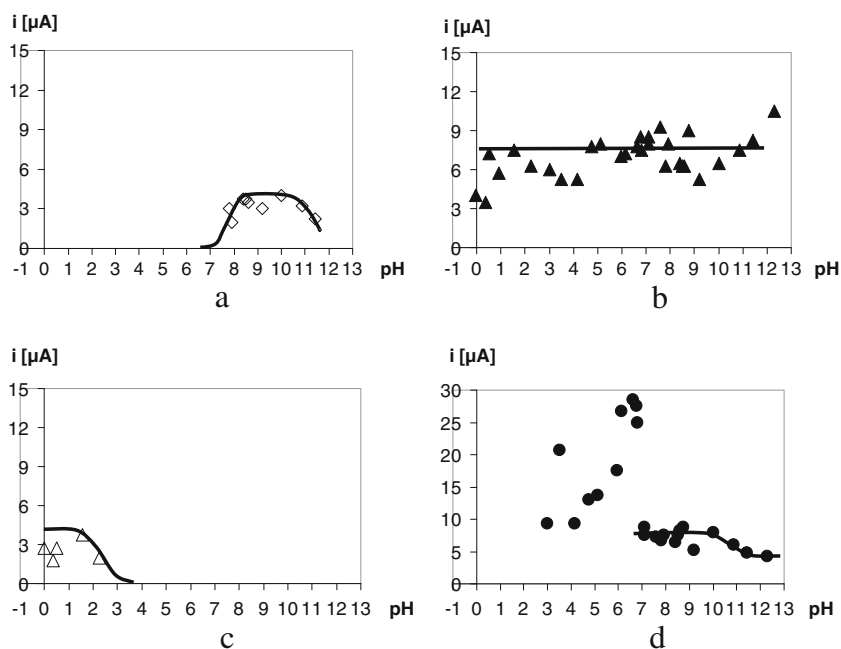
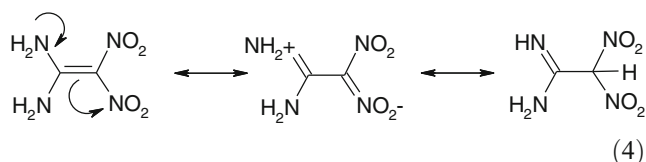


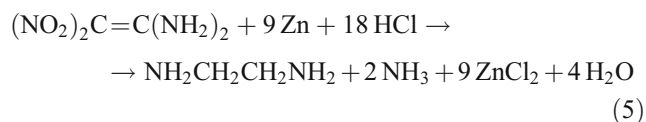
Fig. 3 Plot of the dependences of i vs. pH: **a**=E5, **b**=E6, **c**=E7, **d**=E8 (concentration of FOX-7 3.2×10^{-4} mol/l)



reactions where pH plays a significant role. The complicated reduction pattern as well as the absence of organic amines among products point to the fact that the nitro groups are not reduced in a simple four-electron way yielding the corresponding hydroxylamine according to the expected pattern for α,β -unsaturated nitro compounds [11]. In addition to this, the presence of another nitro group in α -position and pH-sensitive amino groups in β -position enables a.o. tautomeric equilibria, yielding an easily reducible and hydrolyzable imino group.



After a purely chemical reduction of the FOX-7 by zinc in HCl (Šimková L., unpublished results; 0.3 g FOX-7 was dissolved in 25 ml 8% HCl and 3.5 g of zinc powder was added.), ethan-1, 2-diamine as a product was identified. This reduction (5) should involve in total 18 electrons.



When all polarographic limiting currents are summed up at any pH, the total current corresponds always to approx. 18 transferred electrons (by comparison with several standards like *p*-nitrotoluene, *p*-dinitrobenzene or *p*-nitroanisole).

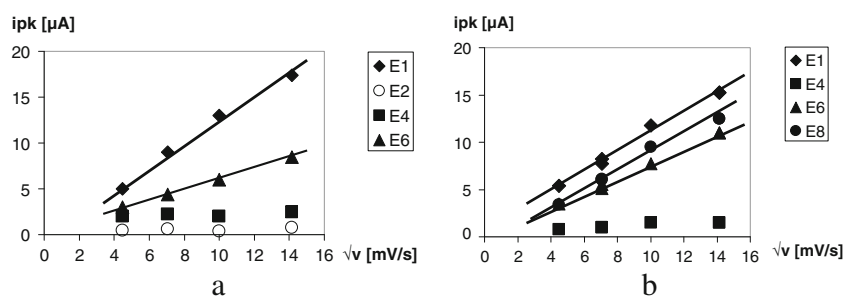
The most significant processes seem to be the waves E1, E6 and E8 appearing in the whole pH range. Whereas the processes E2 and E7 occur only in strongly acidic solutions, the waves E3 and E5 appear only in basic buffers. The reduction step denoted as E4 is represented by small current with a hardly distinguishable shape due to close proximity to other waves. Based on this polarographic study, it is still not possible to assign the recorded reduction waves to the corresponding chemical equations (processes); nevertheless, the mutual comparison of the i vs. pH plots

Table 1 Electroreduction processes E1–E8: pH ranges of their appearance and slopes of their $dE_{1/2}$ vs. dpH dependences

Wave number	pH	$dE_{1/2}$ vs. dpH (mV)
E1	0–1.5	0
	1.5–7.5	87
	>7.5	0
E2	0–1.5	0
	>1.5	140
E3	>7.5	0
E4	0–12	18 ^a
E5	7.5–11.5	0
	0–2	0
E6	2–7.5	87
	7.5–12	0
	>7.5	0
E7	0–2.5	0
E8	0–2	0
	2–7.5	87
	>7.5	0

^a Serious evaluation is difficult

Fig. 4 Plot of the dependences of i vs. \sqrt{v} of all distinguished reduction waves in **a** pH 0.93 and **b** pH 6.13 (concentration of FOX-7 3.2×10^{-4} mol/l)



can suggest connections and relationships between the individual reduction steps that could be used in the next more detailed investigations.

In the pH region between 0 and 7, the first reduction process (E1) exhibited a practically constant limiting current corresponding to five to seven electrons. At higher pH, a decrease of the i vs. pH plot appears, caused probably either by evolution of another, complementary process (E3 or E5, cf. Fig. 2a) or by hydration of one of the present intermediate C=N double bonds [12, 13].

The pH dependence of the potential E6 is very similar to that of E1. In contrast to E1, the current has neither increasing nor decreasing tendency with changing pH (Fig. 3b).

The reduction E8 (Fig. 3d) proceeds at the most negative potentials; therefore, it can be affected by the processes limiting the potential window. An unusually high limiting current with strongly scattered values was repetitively observed of the i vs. pH plot in the pH range between 3 and 7, which is typical for a catalytic process. After reaching pH 7, the limiting current is stabilized to a constant value. This effect is more pronounced at a higher concentration of FOX-7 and is most probably caused by reduction of protons catalysed by the present amino groups.

The eventual mutual relationship between the other processes is still unclear and is being studied.

Cyclic voltammetry

Cyclic voltammetry of 3.2×10^{-4} M FOX-7 at HMDE was performed at pH 0.93; 6.13 and 11.43, using scan rates 20, 50, 100 and 200 mV/s. All processes have irreversible character; no counterpeaks were observed. From the dependence on the scan rate (Fig. 4), it is evident that at least the waves E1, E6 and E8 correspond to diffusion-controlled faradaic processes.

Preparative electrolyses

The results of preparative electrolyses of FOX-7 in acidic media at the mercury pool electrode differ principally from the polarographic ones. Whereas on the polarograms four to

six reduction processes were observed at each pH giving together a current corresponding to 18 electrons, the consumption of electrons during a preparative electrolysis is substantially lower. Depending on the pH and on the applied potential, the apparent value of n (number of transferred electrons per molecule) was 4–7. Moreover, it was proved that the total electrolytic degradation of FOX-7 in acidic media does not depend on the applied potential and can be reached by electrolyzing only at the potential of the first polarographic wave.

The preparative electrolyses were carried out in 5, 0.5 and 0.1 M sulfuric acid at four potentials: -0.25 , -0.4 , -0.8 and -1.05 V. Since the yellow crystalline FOX-7 is hardly dissolved even in acids, the first part of the electrolysis proceeded always in the saturated solution with dispersed crystals of still undissolved substance (this is the reason why the first part of the course of electrolysis depicted in Fig. 5 has galvanostatic character with constant currents of the reduction waves of the parent compound). By application of increased temperature, the fraction of dissolved substrate increased and the electrolysis was sped up. During electrolysis, the solution is being gradually decolorized–bleached.

The electrolytic current is diffusion-controlled. In the solution of completely dissolved FOX-7, the current exponentially decreases until a negligible value is reached (Fig. 6), corresponding to nearly 100% conversion. The electrolysis at -0.25 , -0.4 , -0.8 and -1.05 V proceeded on

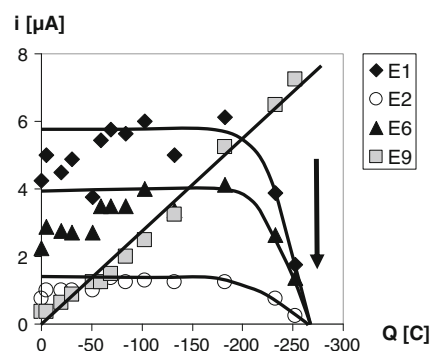
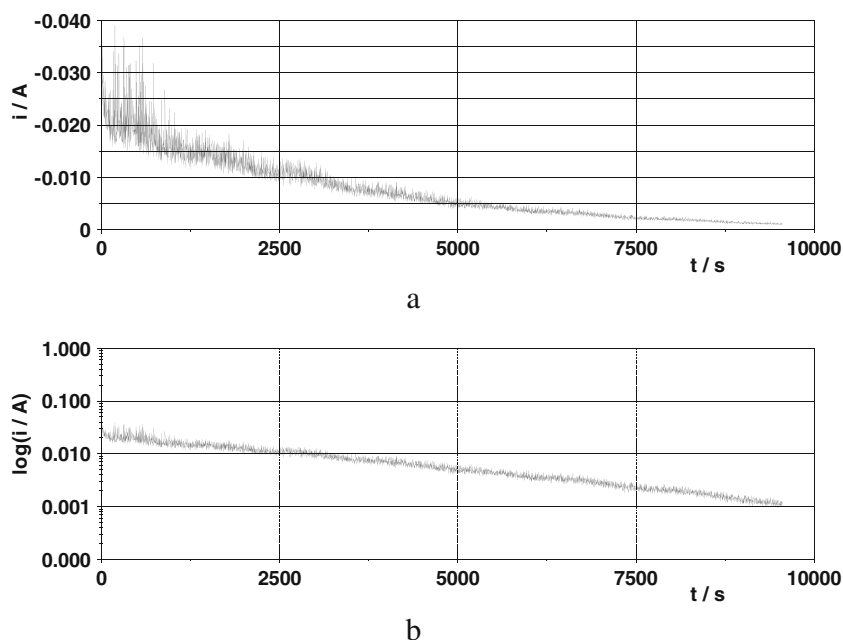


Fig. 5 Plot of individual limiting currents of all main reduction waves during electrolysis of 100 mg of FOX-7 in 0.5 M sulfuric acid at -0.25 V in dependence of passed charge

Fig. 6 The time plot of the passing current during electrolysis (a) and of its logarithm (b) (electrolysis of 25 mg of FOX-7 in 10 ml 5 M sulfuric acid at -0.4 V)



the first sight always in the same way; only the charge passed through the cell depended on the applied potential, whereas at -0.25 V and also at -0.4 V the electron consumption necessary for a total discharge of FOX-7 corresponded to $n=4$, at -0.8 V it was $n=6$ and at -1.05 V the degradation required seven electrons per molecule.

Besides registration of the decreasing electrolytic current, the course of electrolysis was simultaneously monitored by polarography. Samples (40 μ l) were regularly taken from the electrolyzed solution, diluted to 10 ml of sulfuric acid of the same concentration and a polarogram was recorded. An observed simultaneous decrease of the reduction waves E1, E2 and E6 until zero proved a total decomposition of the starting material and the linear development of a new cathodic wave at -0.95 V (E9) demonstrates formation of a stable reducible product (Fig. 5). In the case of diluted sulfuric acid, this behaviour is the same for all three applied potentials of electrolysis.

Interception and identification of products

In order to isolate and identify all products, the solution after electrolyses was neutralized and then evaporated to dryness under mild conditions. The products were first analysed for organic amines using a ninhydrin reaction, but with a negative result. The dried products were extracted by ethylacetate, ethanol and chloroform, respectively, and the extract was checked by thin-layer chromatography; however, neither UV detection nor application of iodine vapours did reveal any individual organic product. Direct NMR and MS analyses were similarly negative, showing only traces

of indistinguishable mixture, probably of higher molecular weight.

Therefore, our attention was turned to eventual gaseous products. A careful observation of the working electrode during electrolysis showed evolution of gases. In the next electrolytic experiments, argon after passing through the solution was collected and analysed. In a “classical” way, the following ions were detected: NH_4^+ (using Nessler test solution) and nitrites (using Griess–Lung reagent) [14]. On the other hand, no presence of CO_2 was found.

For the unambiguous analysis of gases, an “on-line” connected gas chromatograph and mass spectrometer were employed. Figure 7 shows the evolution of N_2 , NO and N_2O during electrolysis of FOX-7 while neither volatile hydrocarbons nor carbon oxides were observed. The

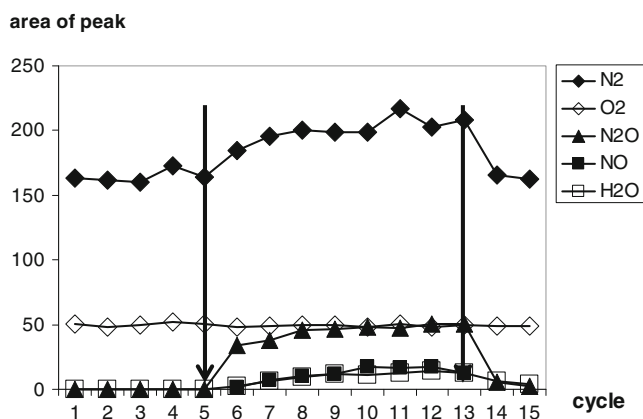


Fig. 7 Time plot of the concentration of gaseous products during electrolysis of FOX-7 in 0.5 M sulfuric acid. The arrows show the start and the end of electrolysis

approximate amounts of gases produced during electrolysis of FOX-7 are N₂ 311 ppm, NO 1,335 ppm and N₂O 313 ppm.

The final solution after electrolysis in 0.1 M sulphuric acid was then neutralized by NaOH and evaporated into GC–MS. The sample was gradually heated up to 120 °C (the rate of heating was 1 K/min). In addition to the abovementioned products, NH₃ was found and the other masses which could be classified as CH₃CH₂OH, NH₂OH, HNO₂ and NaCN were detected. However, unambiguous assignment cannot be done due to the high complexity of mass spectra.

The absence of NO₂ can be explained by the formation of the nitrite anion and/or by the negative oxygen balance (lack of oxygen) in the molecule of FOX-7. The detailed identification of carbon-containing products is a subject of further investigations. The eventual tendency of unsaturated organic intermediates to di- or oligomerize should be considered.

The reducible product E9 was identified by classical qualitative analytical procedure as a nitrite anion and polarographically proved by adding an authentic sample in the solution. This corresponds to the literature data [15, 16] and also it is consistent with our observation that the linear increase of the nitrite wave was found only in diluted (0.1 or 0.5 M) sulfuric acid and not in 5 M sulfuric acid where the nitrite is decomposed to N-oxides.

Conclusions

A new explosive 2, 2-dinitroethene-1, 1-diamine (FOX-7) with the structure containing strong electron donors and electron acceptors in close proximity was for the first time investigated electrochemically. Whereas electrochemical oxidation of this compound does not proceed in accessible potential range, the reduction in aqueous buffered solutions is very complex.

The first significant feature is the difference between the results of polarographic (voltammetric) experiments and exhaustive electrolysis. While the sum of all limiting currents corresponds to the consumption of 18 electrons (which is consistent with the expected formation of ethane-1, 2-diamine), the charge passed during the exhaustive electrolysis and causing the total degradation of the parent compound corresponded only to 4–7 F. These results show the difference between the electroreduction under polarographic conditions, where the relatively short drop time of 2 s gives priority to heterogeneous reduction at the electrode, whereas during

electroreduction under conditions of exhaustive electrolysis the intermediates have time enough for homogeneous follow-up reactions.

The second remarkable finding is that instead of the expected product ethane-1,2-diamine, gases like N₂, N₂O, NO and NH₃ were proved using a.o. the combination EC–GC–MS and, besides that, nitrite anions that are typical for the explosion products were identified.

All these observations suggest that instead of electrochemical reduction, an electrochemically initiated degradation process accompanying the exhaustive electrolysis occurs. This seems to be analogous to the chain of reactions during explosion, which were slowed down by very low concentration and cooled by the solvent. The presented results justify and initiate more detailed mechanistic studies.

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