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Short communication

Electrochemical remediation produces a new high-nitrogen compound from NTO wastewaters

Michael P. Cronin, Anthony I. Day, Lynne Wallace*

School of Physical, Mathematical and Environmental Sciences, University College, University of New South Wales, Australian Defence Force Academy, Northcott Drive, Campbell, ACT 2600, Australia

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Abstract

A new high-nitrogen molecule, identified as azoxytriazolone (AZTO), has been generated in high yield by electroreduction of acidic aqueous solutions of nitrotriazolone (NTO). The near-quantitative conversion appears to be driven by the low solubility of the product. AZTO precipitates readily, leaving the solution virtually free of organic material, and the process may therefore present an efficient and productive remediation method for wastewater from NTO manufacture. The chemical formula and molecular structure of AZTO indicate that it may be effective as an insensitive explosive.

Keywords: Nitrotriazolone; Azoxytriazolone; Wastewater remediation; Insensitive explosives; High-nitrogen compounds

1. Introduction

With many countries now adopting Insensitive Munitions (IM) policies or regulations [1,2], the development and testing of safer explosives has become an important area of research. Insensitive high explosives (IHE) are materials that have low sensitivity to accidental initiation but maintain good explosive performance. Since explosives that are less sensitive also tend to be less powerful, it is important that new compounds exhibiting characteristics of IHE be identified and tested thoroughly.

In addition, environmental issues concerning both the manufacture and the use of explosives are now being addressed. Research continues on “greener” explosives such as the high-nitrogen compounds, which produce less harmful gases on decomposition [3–5], and cleaner methods of synthesis and processing have also attracted attention [6,7]. The environmental effects arising from explosives contamination of soil and water have been well documented [8]. Degradation in the environment is generally slow and initial biotransformation products can be more toxic than the parent nitro compounds, particularly the corresponding amines, which are often carcinogenic [9]. NTO (5-nitro-1,2,4-triazol-3-one) is an insensitive explosive that has shown potential as a safer replacement for RDX, the current military standard. It is already in production in several countries. However, the high aqueous solubility of NTO (up to $15\,\mathrm{g\,L^{-1}}$) [10] means that wastewater from its manufacture cannot be effectively treated by conventional means, such as adsorptive carbon scrubbers. Several alternative methods have been proposed, mainly focusing on advanced oxidation processes or microbial degradation [10–13].

Electrochemical methods of wastewater remediation have the advantage of not requiring any additional chemical loading, since the only input (ideally) is electrical energy. Although oxidative degradation is generally favoured for mineralization of organic pollutants, reductive transformations have also found use, especially for nitro-organics such as TNT [14,15]. In such cases, the reduction products are more amenable to oxidative degradation than the parent compounds. The combined approach of reduction followed by oxidation results in mineralization of the pollutant.

Electroreduction of nitroorganic compounds can produce a variety of products depending on the reaction conditions [16]. Usually, a nitroso intermediate is formed in the first 2-electron step, and this is subsequently reduced to a nitrosamine in a further 2-electron step. At more negative potentials, further reduction to an amine can occur. In some cases, condensation

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* Corresponding author. Tel.: +61 2 62688230; fax: +61 2 62688017.
E-mail address: l.wallace@adfa.edu.au (L. Wallace).

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of the nitroso and the hydroxylamine intermediates can produce an azoxy derivative. The net reaction in this case is a 3-electron reduction of a nitro compound to an azoxy compound (i.e. 3 electrons per mole of nitro compound reduced, or 6 electrons per mole of azoxy compound formed).

This research describes the remediation of aqueous NTO solutions via reductive electrolysis and the resulting electrosynthesis of a new high-nitrogen compound, azoxytriazolone (AZTO). The reduction was found to be effective as a *single-stage* remediation process, without need for subsequent oxidation, since AZTO was formed as a yellow precipitate in high yield and was readily removed by filtration. The remaining solution contained negligible levels of organic material.

2. Experimental

2.1. Materials and methods

NTO was supplied as an aqueous solution ($12\,\mathrm{g\,L^{-1}}$) by Defence Science and Technology Organisation (DSTO). DMSO-d6 was obtained from Novachem pty. Electrosyntheses were carried out using a potentiostat that was built in-house with a ±3 V compliance voltage and 10 A current maximum. A carbon plate working electrode was used, with a platinum basket counter electrode. In some experiments the counter electrode was housed in a separate compartment separated by a porous frit. All electrosyntheses were carried out in $0.1\,\mathrm{mol\,L^{-1}}$ H_2SO_4. Cyclic voltammetry was carried out using an Omni 90 potentiostat. These experiments were performed in $0.1\,\mathrm{mol\,L^{-1}}$ H_2SO_4 using a glassy carbon working electrode, a platinum rod counter electrode and a saturated calomel electrode (SCE) as the reference. All potentials are reported vs. SCE. HPLC analyses were performed on a Shimadzu VP series instrument with SPD-M10AVP diode array detector. A Hypercarb 5 μm column (100 mm × 3 mm) from Thermo Electron Corporation was used, and the mobile phase was aqueous acetonitrile (0–15% concentration gradient) containing 1% trifluoroacetic acid. The method was adapted from that used by Le Campion et al. [10]. UV–vis spectra were measured using a Cary-50 Bio spectrophotometer. NMR spectra were measured on a Varian Unity*plus*-400 spectrometer. Ammonium and nitrate/nitrite concentrations were determined using colorimetry, after AZTO had been filtered from the product electrolyte solution. A procedure based on the Griess reaction was used for nitrate/nitrite. Ammonium ion was determined using Nessler's reagent ($0.09\,\mathrm{mol\,L^{-1}}$ potassium tetraiodomercurate(II) in $2.5\,\mathrm{mol\,L^{-1}}$ potassium hydroxide) [17].

2.2. Electrosynthesis of azoxytriazolone

In a typical divided cell experiment, 200 mL of $0.1\,\mathrm{mol\,L^{-1}}$ NTO in $0.1\,\mathrm{mol\,L^{-1}}$ H_2SO_4 was electrolysed at −1.2 V vs. SCE. Within 15 min the solution, which was initially pale yellow, turned bright green, and after a further 30 min began to turn yellow, at which point a yellow precipitate began to appear. This precipitate continued to be generated, until the current flow in the cell was negligible (approx. 8 h). The yellow solid was then collected by filtration and washed with water, then acetone (yield = 95%). After recrystallization from DMSO/water and further washing with water, the product was oven-dried. HPLC analysis of the filtrate revealed residual NTO (retention time 6.5 min, concentration $<0.005\,\mathrm{mol\,L^{-1}}$) and smaller peaks due to AZTO (5.3 min) and unknown organic material (9.2 and 11 min). Colorimetric analysis showed that trace amounts of ammonium ion and nitrate ions ($<0.005\,\mathrm{mol\,L^{-1}}$) were also present.

Microanalysis: Calcd for $C_4H_4N_8O_3$: C, 22.65; H, 1.90; N, 52.82. Found: C, 22.62; H, 2.12; N, 52.78. Mass spectrum (Electrospray, high resolution in H_2O): MH^+ at $m/z = 213.048$ (Simulation for $C_4H_5N_8O_3^+ = 213.048$). ^{13}C NMR (ppm, d6-DMSO): 154.29, 154.23, 153.62, 145.89, 144.37. ^{1}H NMR (ppm, d6-DMSO, percentage of total intensity given in square brackets): 13.2 (vbr) [19%], 12.73 (br) [6%], 12.48 (br) [26%], 12.44 (br) [26%], 12.08 (br) [23%]. Infra-red Spectrum (KBr disk, major peaks in $\mathrm{cm^{-1}}$): 3170 (br,s), 1682 (vs), 1533 (m), 1466 (m), 1439 (s), 1015 (s), 739 (s), 696 (s). UV/vis (DMSO): $\lambda_{max} = 402\,\mathrm{nm}$; $\varepsilon = 14100\,\mathrm{mol^{-1}\,L\,cm^{-1}}$.

3. Results and discussion

The electrochemical behaviour of NTO was studied by cyclic voltammetry in aqueous $0.1\,\mathrm{mol\,L^{-1}}$ Na_2SO_4. The results are summarized in Table 1.

NTO undergoes an irreversible reduction at −0.40 V (vs. SCE) and an irreversible oxidation at +1.0 V. A second reduction occurs at −0.79 V. Since this peak disappears when the solution is acidified, we believe it is due to a reduction process involving the NTO^- anion. 3-Nitro-1,2,4-triazole (NTr), a structurally similar compound, was also examined under the same conditions. The electrochemistry of NTr has been reported previously, using modified gold or platinum electrodes [18,19]. Under these conditions, reduction of the NTr nitro group to a hydroxylamine occurred in a standard 4-electron step. The similar cathodic response of NTO and NTr in the present work compounds indicates that NTO is also reduced, under these conditions, to a hydroxylamine (i.e. 5-hydroxylamino-1,2,4-triazol-3-one).

For the preparative-scale electrolysis experiments, $0.1\,\mathrm{mol\,L^{-1}}$ H_2SO_4 was used as the electrolytic medium. This was intended to mimic the acidic conditions in current wastewater solutions of NTO. The concentration of NTO in these experiments was also $0.1\,\mathrm{mol\,L^{-1}}$ and the applied

Table 1
Cyclic voltammetry of NTO in aqueous $0.1\,\mathrm{mol\,L^{-1}}$ Na_2SO_4

Compound	pH[a]	Electrode potentials (V vs. SCE[b])
NTO	3.5	E_c(red) = −0.40, −0.79; E_a(ox) = +1.18
NTO	2	E_c(red) = −0.38; E_a(ox) = +0.90
NTr	5	E_c(red) = −0.48, −0.78
NTr	2	E_c(red) = −0.34

[a] Both NTO and NTr are slightly acidic, with pK_a values of 3.76 and 6.05, respectively [20,21]. Solutions were acidified to pH 2 with H_2SO_4(aq).

[b] All peaks were irreversible. For cathodic processes, the cathodic peak maximum (E_c) is cited, and for anodic processes the anodic peak maximum (E_a) is cited.