Short communication

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

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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.
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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 $15\,g\,L^{-1}$) [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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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 ($12 \, \text{g L}^{-1}$) 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 $\pm 3 \, \text{V}$ compliance voltage and $10 \, \text{A}$ 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 $0.1 \, \text{mol L}^{-1}$ H_2SO_4. Cyclic voltammetry was carried out using an Omni 90 potentiostat. These experiments were performed in $0.1 \, \text{mol L}^{-1}$ 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 ($100 \, \text{mm} \times 3 \, \text{mm}$) 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 ($0.09 \, \text{mol L}^{-1}$ potassium tetraiodomercurate(II) in $2.5 \, \text{mol L}^{-1}$ potassium hydroxide) [17].

2.2. Electrosynthesis of azoxytriazolone

In a typical divided cell experiment, 200 mL of $0.1 \, \text{mol L}^{-1}$ NTO in $0.1 \, \text{mol L}^{-1}$ H_2SO_4 was electrolysed at $-1.2 \, \text{V}$ 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 $<0.005 \, \text{mol L}^{-1}$) 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 ($<0.005 \, \text{mol L}^{-1}$) 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. ^1H 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 cm^{-1}): 3170 (br,s), 1682 (vs), 1533 (m), 1466 (m), 1439 (s), 1015 (s), 739 (s), 696 (s). UV/vis (DMSO): $\lambda_{max} = 402 \, \text{nm}$; $\varepsilon = 14100 \, \text{mol}^{-1} \, \text{L cm}^{-1}$.

3. Results and discussion

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

NTO undergoes an irreversible reduction at $-0.40 \, \text{V}$ (vs. SCE) and an irreversible oxidation at $+1.0 \, \text{V}$. A second reduction occurs at $-0.79 \, \text{V}$. 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, $0.1 \, \text{mol L}^{-1}$ 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 $0.1 \, \text{mol L}^{-1}$ and the applied

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

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

[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.

potential was −1.2 V vs. SCE. At this potential, the product was formed more quickly than at less negative potentials; this has also been observed for the electrochemical reduction of TNT in acidic solutions [14]. Competing electrolysis of the dilute sulfuric acid also occurred to some extent. The initial current was typically around 300–400 mA. After a few minutes the pale yellow colour of the NTO solution began to intensify to deeper yellow, and within 45 min a yellow precipitate had begun to appear. After 8 h this precipitate was very thick and the cell current was negligible. The precipitate was filtered off readily. Similar results were obtained in undivided cell experiments, but under these conditions the lower cell resistance meant that the precipitate was formed more quickly (5 h). HPLC analysis of the original filtrate (electrolyte) showed that only small amounts of organic material remained, with residual NTO ($<0.005 \, \text{mol} \, \text{L}^{-1}$) giving the largest peak. Colorimetric analysis revealed trace concentrations of ammonium and nitrate ions ($<0.005 \, \text{mol} \, \text{L}^{-1}$).

The yellow precipitate was characterized as a new compound, azoxytriazolone (AZTO). Microanalysis was consistent with the formula $C_4H_4N_8O_3$, and high-resolution electrospray mass spectrometry confirmed this formula, giving $MH^+ = 213.048$ (simulated for $C_4H_5N_8O_3^+ = 213.048$). AZTO is soluble in DMSO, slightly soluble in water and methanol, and insoluble in other common solvents. The IR spectrum showed a very strong carbonyl peak at $1680 \, \text{cm}^{-1}$ and peaks at 1466 and $1439 \, \text{cm}^{-1}$ consistent with an azoxy group. No melting of AZTO occurred at temperatures up to $400 \,°\text{C}$, though the material darkened in colour at around $300 \,°\text{C}$, indicative of possible decomposition. The yield of the electrosynthesis, based on starting NTO, was almost quantitative.

Electroreduction of nitro compounds to azoxy compounds occurs via condensation of a hydroxylamine with the intermediate nitroso compound [16]. In general, the initially formed nitroso intermediate is more easily reduced than the parent nitro compound, so that further reduction to the hydroxylamine occurs. In this case, the insolubility of the product AZTO provides an additional driving force for the reaction and limits further reduction, and may account for the high yields obtained. The formation of azoxy compounds from nitro explosives has been observed previously, with several azoxy-bridged products being produced from the electrochemical reduction of TNT [14]. Scheme 1 shows the electrolytic formation of AZTO from NTO.

The ^{1}H NMR spectrum in DMSO-d6 displays only rather broad peaks at high chemical shift (12–13 ppm), and all are exchanged on addition of D_2O to the solution. This is consistent with a structure having only N–H protons. There are four main peaks of similar intensity, as expected for the structure comprising two non-equivalent triazolone ring systems, but also one minor peak and evidence of a shoulder on one of the main peaks. All samples displayed the same peaks, even after recrystallization, and all analysed for pure $C_4H_4N_8O_3$, indicating that two very similar structures exist in solution. The ^{13}C NMR spectrum is consistent with this scenario, displaying five peaks, two of which are extremely close (within 0.06 ppm) and one of which is quite broad. The broadness is suggestive of an interconversion process, and we believe this reflects the presence of either
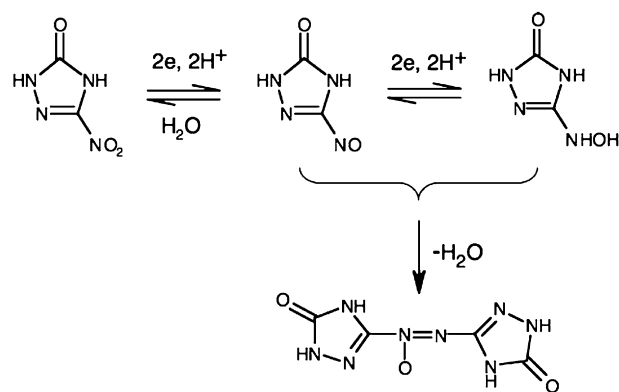
Scheme 1. Electroreduction of NTO in aqueous acid to form AZTO.

tautomers or conformers in solution. Consistent with this interpretation, the addition of two drops of D_2SO_4 to the sample caused the ^{13}C spectrum to simplify to the expected four peaks, with the broad peak becoming sharp. Tautomerism is a common phenomenon in triazoles and triazolones and has been much studied [20,22–26]. Possibilities include keto–enol type tautomerism of the –C(O)NH group in the ring, or structures differing in the position of the ring NH protons (for example, both 1,5H and 2,5H tautomers are found for 4-nitro-1,2,3-triazole in DMSO [22]). In the case of AZTO, conformers can also be envisaged which differ in their capacity for intramolecular hydrogen bonding between the azoxy oxygen and triazolone N–H. The elucidation of the solution behaviour of AZTO is the subject of continuing work in our laboratory.

AZTO has the same chemical formula, and therefore the same oxygen balance, as diaminoazoxyfurazan (DAAF) [27,28], a potential new insensitive high explosive (IHE). Fig. 1 shows the structures of AZTO and related energetic molecules. Oxygen balance, which compares the actual oxygen content of a system with the amount of oxygen theoretically required for complete oxidation, is an empirical indicator of explosive performance—values closer to zero indicate greater power, but also increased sensitivity. IHEs have similar power but reduced sensitivity compared to conventional explosives. Factors that appear to impart extra stability include hydrogen bonding, either intra- or intermolecular, as observed for triaminotrinitrobenzene [29], and resonance stabilization, and more recently,
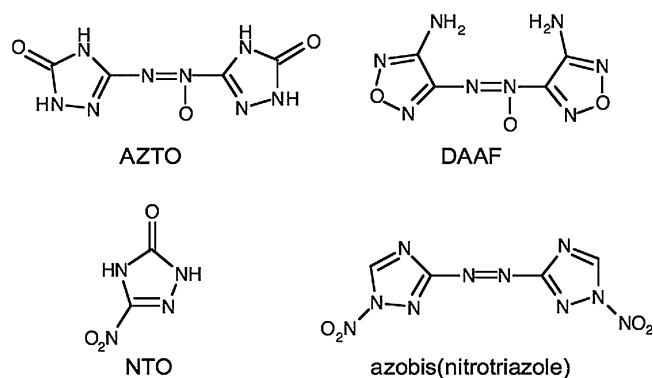

Fig. 1. Structures of AZTO and related compounds.

explosives with high, positive heats of formation have attracted attention [27]. DAAF and AZTO both have lower oxygen balance (−53%) than would normally be considered ideal for a single-component high explosive, but the performance of DAAF has actually been found to be better than that of some IHEs in current use [30]. This high performance has been attributed to its molecular structure, and in particular to the presence of the azoxy group {−N=N(O)−} that forms the bridge between the two rings in the molecule [27]. The azoxy group acts to increase the heat of formation, and hence the overall energy output on explosion. Since AZTO has the same oxygen balance and a similar azoxy-bridged structure to DAAF, it also might exhibit good explosive performance.

An experimental study of the explosive properties of AZTO is beyond the scope of this article. However, we are able to make very simple estimates for heat of explosion, using thermodynamic data derived from the difference method [31], a variation of Benson's well-known group additivity method [32]. Our results for AZTO are given in Table 2, along with other data (including corresponding values for DAAF and NTO). We estimate AZTO to have a positive standard heat of formation (+11 kJ mol^{-1}) and hence a heat of explosion that is less than that of DAAF but comparable to that of NTO. Despite this similarity, only a proper laboratory investigation will ascertain whether the explosive performance of AZTO is similar to NTO. We plan to carry out such a study in the near future.

The high-nitrogen content of AZTO (53% by mass) is a desirable characteristic, as high-nitrogen explosives are becoming increasingly important as "green" alternatives to traditional materials [3–5]. Further chemical adaptation is possible; for example nitration at one or more of the four –NH groups in AZTO, as occurs in the synthesis of azobis(nitrotriazole) from azobis(triazole) [7], would have the effect of increasing oxygen balance and nitrogen content of the material. Chemical modification of DAAF has produced derivatives which also display desirable energetic properties [27,28,38].

AZTO may have other applications, beyond its potential as a new energetic material. Many naturally-occurring azoxy compounds such as azoxybacilin [39] are used as antibiotics or antifungal agents, and some aromatic azoxy compounds have liquid crystal properties [40].

4. Conclusions

Electroreduction of acidic aqueous NTO solutions results in the near-quantitative conversion of NTO to insoluble azoxytriazolone, a new high-nitrogen compound. During this process, soluble organics are almost completely eliminated from the wastewater and no additional chemical loading is required. The high-nitrogen content and molecular structure of AZTO suggest that it may perform well as an insensitive explosive, or serve as a starting material from which further new IHE materials can be prepared. The electrosynthetic process may therefore provide an economically efficient remediation method for wastewater from NTO manufacture.

Table 2
Empirical performance indicators for AZTO and related compounds

Compound	AZTO	DAAF	NTO
Formula	$C_4H_4N_8O_3$	$C_4H_4N_8O_3$	$C_2H_2N_4O_3$
Oxygen balance	−53%	−53%	−24.6%
N content (mass %)	53%	53%	43%
ΔH_f^0(s) (kJ mol^{-1})	+11[a]	+444	−100.8
Heat of explosion (kJ kg^{-1})[b]	2857	4983	2793

[a] Estimated using the difference method [31]. The change in ΔH_f^0 on conversion of 2 mol of a nitro compound to 1 mol of the corresponding azoxy was estimated from comparison of (a) solid aminonitrofurazan (1273 kJ mol^{-1}) and DAAF [33] (increase = 218 kJ mol^{-1}); and (b) gaseous nitrobenzene (68.5 kJ mol^{-1} [34]) and azoxybenzene (342 kJ mol^{-1} [35]) (increase = 207 kJ mol^{-1}). The average difference (213 kJ mol^{-1}) was added to ΔH_f^0 for 2 mol of solid NTO [36].
[b] Calculated from ΔH_f^0 of solid explosive and gaseous products determined using the Kistiakowsky-Wilson rules [37]. Reported value for NTO is 2993 kJ mol^{-1} [36].

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