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Electrochemical reduction of nitrotriazoles in aqueous media as an approach to the synthesis of new green energetic materials[†]

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The synthesis of new azo and azoxy compounds *via* electrochemical reduction of nitrotriazoles has been investigated in aqueous media, using nitrotriazolone (NTO) and nitrotriazole (NTr) as representative substrates. Reduction of NTO produces mainly solid azoxytriazolone (AZTO), with azotriazolone (azoTO) and aminotriazolone (ATO) as minor products, while 3-hydroxylaminotriazole is the major product formed from NTr. AZTO and azoTO are of interest as new green high-nitrogen compounds for use as insensitive high explosives (IHE). The effect of varying reaction conditions such as pH and substrate concentration has been evaluated, and a mechanism is proposed accounting for the experimental observations. In particular, the ratio of azoxy to azo in the solid product is influenced by pH and temperature, and the minor product ATO is formed not *via* direct reduction of NTO but *via* a novel thermal disproportionation reaction of the hydrazotriazolone intermediate. Conditions of high substrate concentration and low cell temperature maximise the azoxy yield and minimise the formation of minor products. Results indicate that this green electrosynthetic approach may be generally useful for the synthesis of new azoxy and azo triazoles from suitable substrates.

Introduction

Green methodologies are increasingly being introduced in the field of energetic materials.¹⁻⁴ In addition to the international move towards insensitive high explosives (IHE), which are safer, less sensitive materials that retain the performance of conventional explosives,⁵ there is now a growing realisation that new explosives also need to be more environmentally friendly. An increasing amount of research has therefore been focused on initiatives to mitigate the environmental impact of the production and use of energetic materials. These approaches range from developing greener methods of synthesis for existing explosives⁶⁻⁸ and treating manufacturing waste,^{3,9} through studies of the environmental fate of explosives,^{10,11} to the design and synthesis of safer and greener end products.^{1,2,4,12–19} One promising approach is to replace some conventional explosives with high-nitrogen compounds. These materials contain a higher proportion of nitrogen by mass, compared to conventional explosives, and they derive their energy output from this factor, rather than via the oxidation of fuel elements (carbon, hydrogen) by oxygen. Since nitrogen gas (N₂) is the major product of explosion, high-nitrogen compounds burn more cleanly than other organic explosives, producing less carbon monoxide, soot and

other incompletely oxidised explosive residues. High nitrogen compounds are used, or are being considered for use, in many applications; for example, as new IHE,^{14,18} as cleaner, cooler burning propellants,¹⁵ and also in some civilian applications, such as gas-generating compounds in vehicle airbags.² Azo, azoxy and hydrazo-based systems comprise one of the more promising classes of high nitrogen compounds,^{14–19} however the current synthetic procedures for these generally utilise strong chemical oxidising or reducing agents, such as potassium permanganate, N-bromosuccinimide, concentrated sulfuric acid and hydrazine monohydrate.^{14–16}

Electrochemical methods of synthesis and waste remediation are increasingly favoured as they are often considered to be economical and environmentally friendly.²⁰⁻²² The use of electrons as reagents avoids introduction of potentially toxic oxidising or reducing agents, reaction conditions are generally mild, and the electrodes can be considered as heterogeneous catalysts, readily re-used. Previously, we reported on the formation of the new high nitrogen compound azoxytriazolone (AZTO), which is produced by electrochemical reduction of nitrotriazolone (NTO) in acidic aqueous solution.²³ NTO is a new insensitive high explosive (IHE) that shows promise as a safer replacement for standard explosive materials in several applications.²⁴ One issue with its manufacture has been the problem of treating the wastewater, since the very high aqueous solubility of NTO means that the wastewater cannot be treated by conventional means. In previous work, we investigated the direct electrolysis of aqueous NTO solutions as a means of

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removing the soluble organic material from waste streams.^{23,25} This research led to the discovery of AZTO, which precipitates from solution in good yield.²³ The structure and formula of AZTO indicated that it also had the potential to be used as an IHE, and preliminary results have confirmed that it responds as a typical IHE in small-scale tests.²⁶ For a typical AZTO sample, the sensitivity to impact and electrostatic discharge (ESD) was identical to that measured for NTO²⁷ (impact Figure of Insensitivity = 100, ESD ignition at 4.5 J not 0.45 J) and the friction sensitivity was lower (> 360 N compared to 252 N for NTO). In particular, AZTO exhibited greater thermal stability than the parent NTO, as is often the case for azoxy and azo materials.¹⁴ Thus, the formation of AZTO from waste NTO solutions could prove to be a very economical method of remediation.

The reduction of NTO to form AZTO is an interesting reaction in itself. While it is well know that the electrochemical reduction of nitrobenzene species can produce azoxybenzenes in some cases (*via* coupling of the initial nitroso and hydroxy-lamine electrode products),²⁸ to date there are very few examples of this type of electrosynthesis in 5-membered heterocyclic systems.²⁹

In the case of AZTO, the efficiency of azoxy formation appeared to be related at least partly to the very low solubility of the product, which precipitated readily from aqueous solution. NMR spectroscopy showed that, despite appearing to be microanalytically pure, AZTO samples contained an unidentified minor species that could not be removed by recrystallisation.

In the present work we report a comprehensive study of the mechanism of this novel electrochemical reaction and the factors influencing product distribution. This is particularly important in optimising the yield of the desired products. A full understanding of these factors will assist in the potential industrial application of a very economical synthesis, and the results are also relevant to laboratory syntheses of potential new high-nitrogen compounds. The minor component present in AZTO samples has been identified as azotriazolone (azoTO), another new high nitrogen compound, and we have found that experimental conditions can favour this species to the extent that it becomes the major component of the solid product. In particular we wished to ascertain whether it was possible to avoid or limit formation of azoTO in the cell, and maximise the yield of AZTO. Some experiments were carried out on nitrotriazole (NTr), a compound structurally similar to NTO and containing a non-exchangeable proton, in order to assist in spectroscopic assignments and to assess the wider applicability of this electrosynthetic reaction in triazole systems. Fig. 1 shows the structures of NTO and NTr, and possible reduction products.

Results and discussion

Upon reduction at -1.2 V vs. SCE in 0.1 mol L⁻¹ H₂SO₄, NTO solutions turned first green, then yellow, before a thick yellow precipitate was formed. NTr solutions turned light blue initially, then pale yellow, and a small amount of yellowishwhite precipitate was formed. The green (NTO) and blue (NTr) colours observed in the initial stages of reduction could be due to intermediate nitroso species, or to anion radicals,



Fig. 1 Structures of (a) NTO (5-nitro-1,2,4-triazol-3-one); (b) NTr (3-nitro-1,2,4-triazole) and possible reduction products (\mathbf{R} = triazolone, triazole): (c) nitroso, (d) hydroxylamine, (e) azoxy, (f) hydrazo, (g) azo, (h) amine.

which would be expected to hydrolyse rapidly in the aqueous medium. For both NTO and NTr, HPLC analysis showed that all substrate was consumed within 5 h.

Identification of reduction products

In the case of NTO, the HPLC chromatogram of the filtered product solution showed a strong peak at 7.0 min corresponding to aminotriazolone (ATO), which was formed in 14% yield. A second, very weak, peak occurred at 3.1 min. This was assigned as hydroxylaminotriazolone on the basis of the UV absorbance profile and the trend in retention times seen for the triazole derivatives (nitro > amine > hydroxylamine, see below). This species was present in very low amounts (<0.5%). There was also a small peak at 0.85 min due to nitrate ion, consistent with some oxidative mineralisation occurring at the counter electrode.

The chromatogram of the final filtered NTr solution showed a peak at 2.9 min due to 3-hydroxylaminotriazole, formed in 81% yield, and traces of a peak at 4.8 min due to aminotriazole (<0.5% yield). The results of typical HPLC analyses are shown in Fig. 2.

The solid product of NTO reduction has previously been identified as azoxytriazolone (AZTO), with a small amount of another species also evident in the NMR spectra.²³ AZTO has significant solubility only in DMSO or neat sulfuric acid. The minor component (15%) in the precipitate was identified as azotriazolone (azoTO), having been isolated in pure form *via* reduction of AZTO (see below), and fully characterised. AZTO and azoTO have close/overlapping peaks in both ¹H and ¹³C NMR spectra in DMSO-d6. Trace amounts (<3%) of hydrazotriazolone (see below) were usually also evident by NMR; this species could be removed by recrystallisation from DMSO-water if necessary. This process does not remove azoTO, which tends to be found in slightly greater proportions in recrystallised material.

The precipitate from NTr reduction had more limited solubility than the NTO product (AZTO and azoTO); neat H_2SO_4 was the only suitable solvent for this material, with D_2SO_4 being used for NMR characterisation. The major component of this precipitate was identified as azotriazole,



Fig. 2 HPLC analysis of the reduction of (a) NTO (circles) to form ATO (squares) and (b) NTr (diamonds) to form hydroxylaminotriazole (triangles). Solid azoxy and azo species removed *via* filtration prior to analysis.

by comparison with an authentic sample prepared by a chemical method.¹⁵ The minor component, which gave rise to two CH peaks in the ¹H NMR spectrum at very similar chemical shift to those for azotriazole, was assigned as azoxytriazole, with the ratio of azo:azoxy being approximately 60:40. The ¹³C spectrum also showed one set of two major peaks and another of four minor peaks, with similar chemical shift to those for AZTO and azoTO. The IR spectrum of the precipitate gave peaks at 1365 and 1338 cm⁻¹, consistent with the azo/azoxy functionality, with the 1365 cm⁻¹ peak being more intense in samples containing a higher proportion of the azoxy compound.

Effect of electrochemical reaction conditions on product distribution

Since the azo and azoxy species derived from both NTO and NTr are of potential interest as energetic materials, a more comprehensive investigation was then carried out to determine the effect of different reaction conditions on the product distribution. In particular, we wished to assess whether it was possible to obtain pure samples of AZTO and/or azoTO by control of the cell parameters. It was also important to ascertain the mechanism by which the azo species is formed, and the source of ATO in the NTO reductions.

Aqueous solutions of NTO or NTr were reduced under different conditions of applied potential, cell temperature, substrate concentration and solution pH. Reactions were followed by HPLC, and any solid products were collected and characterised by NMR spectroscopy. The results are summarised in Fig. 3.

The unassigned consumed substrate ("other") is attributed to a combination of: (1) loss to counter electrode compartment; (2) low concentrations of dissolved species (azo, azoxy and hydrazo) that are not observed by HPLC; and (3) losses through washing of precipitates. Loss of substrate (or dissolved reduction products) can occur through exposure to the counter electrode via diffusion, which is unavoidable. Previous results indicate this can occur at levels of 10-20% in anodic oxidation with a substrate concentration of 0.05 mol L^{-1}).²⁵ UV-vis spectroscopy indicates that AZTO/azoTO is present in product solutions at concentrations representing <2% of NTO consumed under standard conditions. Since these products are not observed by HPLC it seems that they have a strong affinity for the column and are not readily eluted. Oxidative mineralisation is therefore the principal fate of substrate in the unaccounted "other" category, though under certain conditions (see below) more significant concentrations of dissolved azo, azoxy or hydrazo species could also be present.

Electrochemical reduction of NTO. In a 'typical' electrolysis, NTO (10 g L⁻¹) was reduced at -1.2 V in 0.1 mol L⁻¹ H₂SO₄ at room temperature (≈ 20 °C), to give the products described in the preceding section. Under these conditions (Fig. 3A1), ATO accounts for 14% of the NTO consumed, and the precipitate accounts for a further 69% (solid contains AZTO and azoTO in 5.7:1 ratio).

Effect of cell potential. As further reduction of AZTO was considered to be the most likely source of azoTO, the minor component in the solid product, it was necessary to establish whether this could be prevented or limited by use of a lower cell potential. Cyclic voltammetry has shown that reduction of NTO occurs at -0.38 V in acidic solution,²⁵ well below the cell potential of -1.2 V typically used in our experiments. No further peaks were observed in the voltammogram before -1.4 V, where the solvent front began. However, when a lower applied potential of -0.4 V was used in the bulk electrolysis, a slightly higher proportion of azoTO was found in the cell precipitate (AZTO: azoTO = 4.3:1, Fig. 3A2). The reduction proceeded more slowly at the lower voltage and, importantly, ATO was formed in solution to approximately the same extent. This result suggests ATO is not formed *via* further reduction of



Fig. 3 Fate of substrate (A) NTO and (B) NTr upon reductive electrolysis under different cell conditions: (1) Standard conditions (0.077 M substrate in 0.1 mol L^{-1} H₂SO₄, T \approx 20 °C, -1.2 V); (2) Applied potential = -0.4 V; (3) Cell temperature = 5-10 °C; (4) [Substrate] = 0.0077 mol L^{-1} ; (5) Supporting electrolyte = 0.1 mol L^{-1} Na₂SO₄.



Fig. 4 Cyclic voltammograms of (a) AZTO and (b) NTO in DMSO (0.1 mol L^{-1} TBABF₄. Dotted lines show the effect of added 0.1 mol L^{-1} H₂SO₄(aq).

the hydroxylamine intermediate, since the reduction of hydroxylamine to amine normally occurs at a potential considerably more negative than that for reduction of nitro to nitroso/hydroxylamine.²⁸ In addition, this result shows that further reduction of AZTO to azoTO cannot be eliminated by use of a lower cell potential.

Cyclic voltammetry of both AZTO and NTO in DMSO (Fig. 4) showed that the reduction peaks occurred at very similar potentials of -0.76 and -0.72 V vs. Ag/AgCl. (DMSO is the only suitable solvent in which a measurable concentration of AZTO could be achieved). To provide some insight into the likely behaviour in aqueous acid, several drops of 0.1 mol L⁻¹ H₂SO₄ were added to the voltammetric solutions. This caused an anodic shift in both peaks but the potentials remained very close (-0.67 and -0.61 V respectively).

This supports the observations found in the bulk electrolysis experiments: during the reduction of NTO, further reduction of AZTO cannot be avoided by control of the cell potential.

Effect of lower cell temperature. We then considered that cooling the cell might enhance precipitation of solid AZTO component, thereby inhibiting further reduction. When the bulk reduction was carried out at 5–10 °C on an ice bath, it was found that the formation of azoTO was indeed inhibited, with the precipitate comprising AZTO: azoTO in 19:1 ratio (Fig. 3A3). The overall yield of precipitate was higher (87%) than obtained at room temperature, and much less ATO was formed in solution (1%).

Effect of substrate concentration. With a much lower NTO concentration of 1 g L^{-1} (Fig. 3A4), ATO was formed in solution to a greater extent (24%). The precipitate was formed in lower yield (36%) and contained a much higher proportion of azoTO (1:5.7 AZTO:azoTO). Under these conditions, dissolved AZTO represents a much greater proportion of the total generated, so that further reduction can become more significant. At these concentrations, dissolved AZTO, azoTO

and possibly hydrazotriazolone may then contribute more significantly to the "other" category.

Effect of increased cell pH. In electrolyses carried out at higher pH (initial pH = 2, final pH = 6–7), with 0.1 mol L^{-1} Na₂SO₄ as electrolyte (Fig. 3A5), azoTO again became the dominant component of the solid product (1:1.6 AZTO: azoTO) and ATO was formed to a greater extent (39% based on starting NTO). The overall yield of solid product (24%) was much lower than in the acid experiments.

Electrochemical reduction of NTr. Bulk electroreduction experiments were also carried out on solutions of NTr, to assess whether the observations made for NTO were applicable to other nitroazoles. The results are shown in Fig. 3B1–B5.

Reduction of NTr occurred efficiently and at a similar rate to reduction of NTO, but in this case the major product of reduction was identified as hydroxylaminotriazole, a soluble species which was isolated as the sulfate salt and fully characterised. This observation is in agreement with the work of Kokkinidis *et al.*,³⁰ who reported on the voltammetric behaviour of NTr on platinum-modified electrodes. In the present case, a small amount of precipitate was also formed, comprising azo-and azoxytriazole (3%).

The effect of reaction conditions on the precipitate mirrored the results obtained for NTO: use of a lower temperature gave a higher yield of precipitate and increased the proportion of azoxy to azo (B3); and electrolysis at higher pH also increased the amount of azoxytriazole in the precipitate (B5). However, in all cases the hydroxylamine was the major product of reduction. Aminotriazole was produced only in low amounts. This is consistent with the conclusion drawn for NTO: that further reduction of hydroxylamine directly to amine does not occur at the cell potentials used in this study. It also accords with previously reported voltammetric results,²³ which show no reductions for NTr between -0.4 and -1.4 V. As observed for NTO, lower substrate concentration (B4) and higher pH (B5) resulted in slightly higher concentrations of the amine.

Electrochemical reduction of AZTO. To obtain further information on the mechanism of further reduction of AZTO, and the likely source of ATO, bulk reduction experiments were carried out on AZTO (samples containing $\approx 15\%$ azoTO) in 0.1 mol L⁻¹ Na₂SO₄(aq). In these experiments, the initial solution was adjusted to pH 7–8 by addition of concentrated NaOH(aq) to achieve sufficient solubility of the starting AZTO. At alkaline pH, AZTO dissolves fully due to deprotonation.

¹H NMR spectroscopy in DMSO showed that this crude product consisted of a small amount of azoTO and another major product displaying 3 proton environments of equal intensity. This second species was present in variable proportions in different batches, and in one case was formed exclusively. This allowed the species to be identified as hydrazotriazolone, confirmed by microanalysis and mass spectrometry. When the NMR solution was heated strongly, hydrazotriazolone peaks decreased, while the amount of azoTO increased and new peaks appeared due to the formation of ATO. This raised the possibility that ATO was produced from hydrazotriazolone *via* a disproportionation reaction (eqn (1)).

$$2 \text{ R}-\text{NH}-\text{NH}-\text{R} \rightarrow \text{R}-\text{N}=\text{N}-\text{R} + 2 \text{ R}-\text{NH}_2 \qquad (1)$$

To test this hypothesis, reduction of AZTO was repeated and the final aqueous solution was divided into two equal portions: one was immediately acidified to pH ≈ 2 (giving precipitate X, 0.116g), and the other was heated to 80 °C for ca. 5 min before being cooled and acidified (giving precipitate Y, 0.056 g). NMR spectroscopy showed that ppt X comprised hydrazotriazolone and azoTO in a 9.6:1 ratio, while ppt Y consisted of only azoTO. The molar ratio of hydrazotriazolone in ppt X to azoTO in ppt Y was 2:1 as expected from eqn (1). HPLC analysis showed that in the filtrate of the heated portion (filtrate Y) the concentration of ATO had increased almost 5-fold compared to the unheated portion. However for both portions, the molar ratio of ATO: azoTO was approximately 2:1, again as expected from eqn (1). Almost identical product ratios were obtained when the above thermal procedure was carried out under an inert atmosphere, demonstrating that aerial oxidation of hydrazotriazolone is not a significant reaction pathway here.

Thermal disproportionation of hydrazobenzenes to form azo compounds and amines has been reported previously,^{31–33} but this appears to be the first example of such a transformation involving 5-membered heterocyclic systems. The results suggest this thermal reaction is the source of ATO and the principal, if not only, source of azoTO in the reduction of NTO, with hydrazotriazolone being the major product of reduction of AZTO in alkaline solution. Since the hydrazotriazolone intermediate is not a major component of precipitates formed in acid electrolyses, but both azoTO and ATO are produced in significant amounts, it appears that the disproportionation rate may be enhanced in acid solution (H⁺ catalysis). Fig. 3 shows that the molar ratio of ATO: azoTO is generally also around 2:1 in room temperature acid solution (A1, A2, A4), consistent with this hypothesis.

Proposed reaction mechanism

The results obtained can be explained in terms of the reaction mechanism presented in Scheme 1.

In acidic solution, the major product formed on reduction of NTO is the azoxy derivative, AZTO. Thus, the coupling of nitroso and hydroxylamine derivatives is clearly very efficient in this case. Further reduction of AZTO can occur to some extent, producing azoTO and ATO as the final products, but this is limited by the low solubility of AZTO. If the cell is cooled, precipitation of solid AZTO is enhanced and the extent of further reduction is minimised by the lower solution concentration of AZTO. It is not possible to prevent further reduction by control of cell voltage, as the reduction potentials of NTO and AZTO are very similar.

At higher pH, further reduction of AZTO occurs to a much greater extent. This is probably due to its increased solubility, especially in the vicinity of the working electrode where the local pH is likely to be higher than the bulk solution.²⁸ Any conditions that increase the *proportion* of AZTO in solution (increased temperature, pH or decreased substrate concentration) serve to increase the extent of further reduction. Upon reduction of AZTO, the main electrode product is hydrazotriazolone, which then undergoes a thermal disproportionation



Scheme 1 Proposed mechanism for reduction of nitrotriazoles, showing possible major reaction pathways. Dotted arrows represent possible minor pathways. Blue arrows correspond to electron transfer steps, and red arrows to thermal reactions.

reaction to produce azoTO and ATO. This reaction results in a much lower yield of solid product, since soluble ATO is formed in up to 40% yield. The results indicate that the disproportionation reaction of hydrazotriazolone is the only source of ATO, and the major source of azoTO, in the reduction of NTO. It is possible that some direct reduction of AZTO to azoTO also occurs to a limited extent.

On reduction of NTr, the major product formed is hydroxylaminotriazole, with very low yields of the azoxy or azo species being formed. This indicates that the coupling of the initial electrode products, the nitroso and hydroxylamine derivatives, is much less efficient in this case. In nitrobenzenes, the coupling reaction occurs between the protonated nitroso derivative and the unprotonated hydroxylamine.²⁸ The efficiency of this step depends on the concentrations achieved by both of these species, and is therefore related to the pK_a values for both. NTr has a much higher pK_a value (6.05³⁴) for the ring NH protons than NTO (3.76^{35}) . It therefore appears likely that the pKa values for the relevant nitroso and/or hydroxylamine groups are less favourable for coupling in the case of NTr. Although in this case the amine is formed to only a small extent, the higher concentrations of this species observed under conditions of dilute substrate (Fig. 3B4) and higher solution pH (Fig. 3B5) follow the same trend as observed in the NTO reactions, implying that a similar mechanism is likely to operate here.

These results suggest that while the electrochemical formation of azo- and/or azoxytriazoles is possible, the efficiency depends on the particular substrate. In the case of NTO, the coupling reaction between the nitroso and hydroxylamine derivatives is highly favoured, but the corresponding species for NTr react only slowly.

Current efficiency of AZTO synthesis

In an electrosynthesis the current efficiency of the reaction is an important economical factor. Table 1 shows the current efficiency of AZTO electrosynthesis at different applied cell potentials, expressed as the charge passed in forming AZTO as a percentage of the total charge passed. The current efficiency for the total solid product (AZTO plus azoTO) is also shown. At higher cell potentials the product is formed more quickly as expected, but the current efficiency decreases. Optimum current efficiency was achieved with an applied cell potential of -0.6 V (*vs.* SCE) and at low temperature (5–10 °C). Under these conditions the yield of solid AZTO was 71%, formed with a good current efficiency of 71%. Based on the total yield of solid product, the current efficiency here is 80%.

Conclusions

Electrosynthesis could be a valuable and environmentally friendly approach to the synthesis of new high nitrogen compounds as green energetic materials, using clean methodology, mild conditions and aqueous media. In particular, the electrochemical technique may prove to be a highly economical method of treating NTO waste. Three different species (AZTO, azoTO and ATO) are produced from the reaction, all of which have useful energetic properties. Reaction conditions can be chosen to maximise the yield of AZTO (high NTO concentration, low temperature). In a slightly cooled cell the conversion of NTO to AZTO occurs with very high efficiency. AzoTO and hydrazotriazolone can be produced by direct reduction of AZTO. These materials have potential for use as IHE by themselves, or might act as substrates for nitration to produce gas-generating solids.

The mechanism of the reduction follows one of the standard pathways expected for nitrobenzenes, but to date there are very few examples of electrochemical azo/azoxy synthesis in 5-membered heterocycles-we are aware of only two other examples.²⁹ The final product distribution is strongly influenced by substrate concentration, reaction pH and temperature. In the case of NTO, the high yield of AZTO is due partly to the low solubility of this species, which limits further reduction to hydrazo and azo derivatives. The NTr experiments show that the method can be applied to other triazoles, with a similar overall reaction mechanism being observed. However the yield of the desired azo and azoxy products is highly dependent on the particular substrate. Current work in our laboratory is focussed on the electrochemical reduction of further heteroaromatic nitro compounds to form new azo and azoxy derivatives, also under aqueous conditions.

This work has identified the new high-nitrogen compounds azotriazolone and hydrazotriazolone, in addition to the previously reported AZTO. These materials have potential for use as energetic materials or as substrates for production of new energetic materials.¹² In addition, salts of aminotriazolone

V (vs. SCE)	$T/^{\circ}\mathrm{C}$	t ₉₉ (min) ^a	% Yield AZTO	% Yield azoTO	CE ^b per mol AZTO (plus azo) formed
-0.4	20-25	600	51	12	51% (61%)
-0.6	20-25	380	59	10	57% (65%)
-0.6	5-10	480	71	11	71% (80%)
-1.2	20-25	200	58	10	42% (48%)
-1.2	5-10	420	82	4	52% (53%)

^{*a*} Time for >99% consumption of NTO. ^{*b*} Current efficiency, based on 6 Faraday per mol AZTO formed, and 10 Faraday per mol azoTO formed (*via* hydrazotriazolone, see Scheme 1).

or hydroxylaminotriazole could be utilised in the form of ionic liquids; for example, ionic liquid triazolammonium salts are currently of interest as desensitising additives for some explosives formulations.³⁶

Experimental

Materials and methods

NTO was supplied as an aqueous solution (10 g L⁻¹), by Defence Science and Technology Organisation (DSTO, Edinburgh, SA, Australia). 3-nitro-1,2,4-triazole, 3-amino-1,2,4-triazole, palladium charcoal, sulfuric acid (98%), sulfuric acid-d2, DMSO-d6, HPLCgrade acetonitrile, spectrophotometric grade trifluoroacetic acid (TFA) and Na₂SO₄·10H₂O were obtained from Sigma-Aldrich, and high-purity argon from BOC gases. Other reagents were obtained from Ajax fine chemicals. A sample of azotriazole was prepared by oxidation of aminotriazole, in an adaptation of the method of Sivabalan *et al.*¹⁵

Electrochemistry: Preparative-scale electrolyses were carried out using a potentiostat that was built in-house, which had a ± 3 V compliance voltage and 10 A current maximum. A double carbon plate working electrode was used (dimensions 2.5×4.5 cm), with a platinum basket counter electrode (gauze dimensions 1.2 cm $\times 4.7$ cm) and a saturated calomel reference electrode (SCE). The counter electrode was housed in a separate compartment separated by a porous frit. Cyclic voltammetry was carried out using an eDAQ EA161 potentiostat operated *via* an eDAQ ED401 e-corder. A glassy carbon working electrode, platinum wire counter electrode and Ag/AgCl reference electrode were used, and the supporting electrolyte was 0.1 mol L⁻¹ Na₂SO₄.

Chromatography: HPLC analyses were performed on a Shimadzu VP series instrument with SPD-M10AVP diode array detector. A Hypercarb 5 μ m column (100 mm \times 3 mm) from Thermo Electron Corporation was used. The method was adapted from that used by Le Campion *et al.*³⁷ The elution gradient consisted of: t_{0-5min} : 1% aqueous TFA; t_{10-20} : 15% acetonitrile in 1% aqueous TFA; t_{25-30} : 1% aqueous TFA.

Samples were extracted during electrolysis and left to stand for at least 24 h to allow any solid material to settle, before HPLC analysis was conducted on the diluted aliquots. Standard solutions were using in quantifying NTO (retention time 12.1 min), ATO (7.0 min), NTr (11.0 min), 3-aminotriazole (4.8 min) and 3-hydroxylaminotriazole (2.9 min). Hydroxylaminotriazolone (3.1 min) was estimated by assuming a response factor similar to that of NTO and ATO (average value). Molar absorptivities of NTO and ATO are similar at 200 nm in aqueous acid (respectively 3900 and 3400 mol⁻¹ L cm⁻¹).

FTIR spectra were collected as KBr disks on a Shimadzu IRPrestige-21 FTIR spectrometer, at a resolution of 4 cm⁻¹. NMR spectra were measured on a Varian Unity*plus*-400 spectrometer.

Preparative scale electrolyses

In typical reactions, 250-mL solutions of the substrate (NTO or NTr) in either 0.1 mol L^{-1} H₂SO₄ or 0.1 mol L^{-1} Na₂SO₄ were reduced for 5–8 h depending on time required for consumption of substrate. Some reactions were monitored

by HPLC. NTO was used as supplied (10 g L^{-1} , 0.077 mol L^{-1}), and NTr solutions were also prepared to 0.077 mol L^{-1} . Precipitates formed during electrolysis were collected by filtration, washed with water and ethanol and dried at 80 °C.

Electrosynthesis of azoxy-1,2,4-triazole-3-one (AZTO). The initially colourless NTO solutions turned green within 15 min and then yellow. AZTO was produced as a thick yellow precipitate. Yields: typically 65–90%, with higher yields obtained at low cell temperature (5–10 °C). Mp > 300 °C. Microanalysis (for a sample comprising 85% AZTO and 15% azoTO by NMR): Found: C, 22.3; H, 2.1; N, 52.3%; Calc for (C₄H₄N₈O_{2.85}·0.5H₂O): C, 22.3; H, 2.3; N, 52.0%. IR spectrum: ν_{max}/cm^{-1} 3050, 2805, 1665, 1575, 1536, 1466, 1438, 1361, 1314, 1258, 1200, 1132, 1122, 1028, 1013, 997, 808, 785, 735, 693, 664. $\delta_{\rm H}$ (400 MHz, DMSO-d6): 12.08 (1H, br, NH), 12.44 (1H, br, NH), 12.48 (1H, br, NH), 13.2 (1H, vbr, NH). Small peak at 12.74 ppm corresponds to azoTO (see below). $\delta_{\rm C}$ (400 MHz, DMSO-d6): 144.41, 145.96, 153.67, 154.32. Smaller peaks at 154.38 and 154.25 ppm correspond to azoTO (see below).

Electrosynthesis of hydrazo-1,2,4-triazol-3-one. AZTO (0.5 g) was suspended in 0.1 mol L^{-1} Na₂SO₄ (200 mL), and concentrated NaOH(aq) was added to pH8, when most substrate had dissolved. The solution was electrolysed at -1.2 V for 8 h. The pH of the solution increased steadily, and was periodically adjusted to \approx pH8 by dropwise addition of conc. H₂SO₄. The final orange-yellow solution was acidified to pH2 by addition of conc. H₂SO₄, giving a thick yellow precipitate (60-70% yield). Typically, this solid product comprised hydrazotriazolone plus azoTO (azoTO present at 10-30% by NMR), but a high-purity sample of hydrazotriazolone was obtained in one instance, allowing full characterisation of this species. Mp 180 °C dec. Microanalysis: Found: C, 21.4; H, 3.05; N, 50.55%; Calc for C₄H₆N₈O₂:1.25H₂O: C, 21.8; H, 3.9; N, 50.8%. IR spectrum: $\nu_{\rm max}/{\rm cm}^{-1}$ 3200, 3094, 3030, 2864, 1734, 1618, 1466, 1443, 1292, 1128, 1053, 1024, 793, 712, 664, 583, 509. $\delta_{\rm H}$ (400 MHz, DMSO-d6): 7.97 (2H, br, NH-NH), 10.40 (2H, br, NH), 10.87 (2H, br, NH). δ_C (400 MHz, DMSO-d6): 149.47, 155.21. Mass spectrum (ESI): $MH^+ m/z$ 199.1.

Electrosynthesis of azo-1,2,4-triazol-3-one (azoTO). The above procedure for electrosynthesis of hydrazotriazolone was followed. The final yellow solution was heated to 80 °C for 5 min, allowed to cool, and acidified to pH2 with conc. H₂SO₄. This produced azoTO as a yellow precipitate in 25% yield. Mp > 300 °C. Microanalysis: Found: C, 24.3; H, 2.05; N, 57.1%. Calc for C₄H₄N₈O₂: C, 24.5; H, 2.1; N, 57.1%. IR spectrum: ν_{max}/cm^{-1} 3040, 2955, 2831, 1670, 1541, 1470, 1428, 1293, 1119, 1041, 1016, 809, 743, 699, 670. $\delta_{\rm H}$ (400 MHz, DMSO-d6): 12.44 (br, 2H, NH),12.74 (br, 2H, NH). $\delta_{\rm C}$ (400 MHz, DMSO-d6): 154.28,154.40.

Electrosynthesis of azoxy-1,2,4-triazole/azo-1,2,4-triazole. A pale yellowish-white precipitate was formed during electrolysis of NTr. Yields were 3–20%, depending on conditions (see text). Precipitate comprised a mixture of azotriazole and azoxytriazole and very poor solubility prevented separation of these. Mp > 300 °C. Microanalysis on sample comprising 60:40 azo: azoxy: Found: C, 24.9, H, 2.9, N, 60.3%. Calc for C₄H₄N₈O_{0.4}·H₂O: C,

25.5, H, 3.2, N, 59.4%. IR spectrum: ν_{max}/cm^{-1} 3111, 3022, 2875, 2777, 1475, 1365*, 1339, 1273, 1175, 1117, 1030, 972, 908, 768, 741, 648, 577, 436. *This peak was stronger in samples containing a higher proportion of the azoxy component. $\delta_{\rm H}$ (400 MHz, D₂SO₄, DMSO-d6): azoxytriazole: 8.85 (1H, s, CH), 8.98 (1H, s, CH); azotriazole: 8.95 (2H, s, CH). $\delta_{\rm C}$ (400 MHz, D₂SO₄, DMSO-d6): azoxytriazole: 156.4, 153.4, 149.0, 146.2; azotriazole: 162.1, 148.0.

Electrosynthesis of 1,2,4-triazol-3-hydroxylammonium sulfate. The acidic filtrate from electrolysis of NTr (above) was evaporated to near dryness, producing a pale yellow crystalline solid, which was collected by filtration and washed with a little cold water. The crude product (1.03 g, 36%) was recrystallised several times from water-ethanol, washed with ethanol and dried at 80 °C overnight. Mp 170–172 °C dec. Microanalysis: Found: C, 16.3; H, 3.7; N, 38.6%. Calc for (C₂H₅N₄O)₂SO₄: C, 16.1; H, 3.4; N, 37.6%. IR spectrum: ν_{max}/cm^{-1} 3242, 3127, 2872, 2690,1662, 1510, 1369, 1335, 1256, 1161, 1111, 1086, 1065, 980, 945, 878, 830, 768, 716, 698, 677, 636, 611, 548, 507. δ_{H} (400 MHz, DMSO-d6): 8.03 (1H, s, CH). δ_{C} (400 MHz, DMSO-d6): 157.85, 144.39. Mass spectrum (ESI-HR) MH⁺ *m/z* 101.046.

Synthesis of 1,2,4-triazol-3-one-5-amine (ATO). This material was initially prepared by chemical reduction of NTO, via an adaptation of the method described by Le Campion et al.³⁷ and was also obtained via reduction of AZTO using a similar procedure. Pd/C was added to either (a) a solution of NTO in water/methanol (1.5:1), or (b) a suspension of AZTO in water/methanol (1.6:1; the solid gradually dissolved). The vessel was then placed under an atmosphere of H₂ gas (1 atm) and the mixture shaken for several hours. The final mixture was filtered through celite and the solvent evaporated. The crude product was recrystallised from ethanol-water. The product of NTO reduction was yellow, as described in reference 37, and the ¹H NMR spectrum (not previously reported) showed that it contained small amounts of azoTO and hydrazotriazolone, in addition to the major peaks (listed below). The product of AZTO reduction was white, and no impurities were evident by ¹H NMR spectroscopy. The IR spectra of the two batches were identical. The melting point for the white solid was higher than reported in reference 37 (240–245 °C)³⁷ but agreed well with the value given in an earlier report of the material, prepared via a different method.³⁸ Characterisation data are given for the white solid ATO. Yield (from AZTO) = 47%. Mp 285 °C (dec), $(\text{lit.}^{38} 286-290 \text{ °C})$ (dec). Microanalysis: Found: C, 23.4, H, 4.2, N, 56.6%. Calc for C₂H₄N₄O: C, 24.0, H, 4.0, N, 56.0%. IR spectrum: ν_{max} cm⁻¹ 3397, 3188, 2914, 2826, 2671, 1694, 1647, 1522, 1420, 1354, 1302, 1148, 1040, 1017, 853, 800, 750, 702, 675, 573. $\delta_{\rm H}$ (400 MHz, DMSO-d6) 5.25 (2H, br, NH₂), 10.04 (1H, br, NH), 10.27 (1H, br, NH). $\delta_{\rm C}$ (400 MHz, DMSO-d6) 147.9, 155.2 (lit.³⁷ 147.8, 155.1). Mass spectrum: $M^+ m/z = 100.0$.

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