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Full Paper

Electrochemical detection of explosive compounds in an ionic liquid in mixed environments: Influence of oxygen, moisture and other nitroaromatics on the sensing response

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(Invited contribution for the *special issue in memory of Ken Seddon*)

Abstract

From a security point of view, detecting and quantifying explosives in mixed environments is required to identify potentially concealed explosives. Electrochemistry offers a viable method to detect nitroaromatic explosive compounds due to the presence of easily reducible nitro groups that give rise to a current signal. However, their reduction potentials can overlap with interfering species, making it difficult to distinguish particular compounds. We have therefore examined the effect on the cyclic voltammetry (CV) and square wave voltammetry (SWV) of nitroaromatic compounds in a range of mixed environments, focusing on 2,4,6-trinitrotoluene (TNT) and 2,4-dinitrotoluene (DNT) as model analytes, and using the hydrophobic room temperature ionic liquid (RTIL) $[P_{14,6,6,6}][NTf_2]$ as the solvent. The effect of oxygen, moisture and other nitroaromatic species on the cyclic voltammetry and square wave voltammetry signatures is studied. Oxygen (0–20 % vol.) minimally affects the current of the first reduction peak of TNT in $[P_{14,6,6,6}][NTf_2]$, but significantly affects the current for DNT. The impact of water (0 to 86 % relative humidity), however, was much more dramatic – even in the hydrophobic RTIL, water significantly affected the currents of the analyte peaks for TNT and DNT, and gave rise to additional reduction features, further contributing to the current. Additionally, the voltammetry of other related di- and tri-nitro compounds (2,6-dinitrotoulene, 1,3-dinitrobenzene, 2,4,6-trinitrotoluene, 1,3,5-trinitrobenzene and musk xylene) was also studied to understand how different substituents on the aromatic ring may affect the reduction potentials. A 50:50 mixture of TNT and DNT revealed that both analytes could be identified and quantified separately, using square wave voltammetry. Overall, this information is useful to determining the effect of other species on the current signals of electrochemical explosive sensors, and reveals that it may be necessary to dry the aprotic RTIL electrolyte when used in humid environments.

Introduction

Room temperature ionic liquids (RTILs) are an interesting class of ionic materials that have been employed in a diverse range of applications over the last two decades.[1-8] They are particularly attractive as electrochemical solvents due to their many advantageous properties, including wide electrochemical windows, intrinsic conductivity, high chemical and thermal stability, low (or near zero) volatility, high polarity and good solvation abilities.[9-11] Unsurprisingly, many researchers use RTILs for fundamental electrochemical studies to understand more about reaction mechanisms and solvation effects of dissolved

species,[10-12] and also for electrochemical sensing applications.[13-17]

Most experiments reporting the sensing of analytes in RTILs take place under dry and inert gas "ideal" environments, and provide a wealth of information about the sensing mechanisms and the behaviour of analyte species under controlled conditions.[10] However, if RTIL-based electrochemical sensors are to be implemented in real applications in the field, the sensor may be required to operate in an air (oxygenated) background, and in a wide range of humidity levels. Zeng and co-workers recently reported the detection of gaseous analytes under both aerobic and anaerobic conditions,[18-19] and others have reported the electrochemical behaviour of species in atmospheres with different levels of humidity,[20-21] but there is still much information lacking in this area. It is known that water dramatically influences the electrochemical windows of RTILs,[22] and alters the diffusion coefficients of dissolved species,[23] so the knowledge of the electrochemical behaviour in humid environments is important.

In this work, two explosive compounds – 2,4,6-trinitrotoluene (TNT) and 2,4-dinitrotoluene (DNT) – are chosen as model analytes, to study the effect of atmospheric impurities (oxygen/air and moisture) in RTILs on the electrochemical response. TNT is widely used in the manufacture of explosives for military purposes, and is known to be an environmental contaminant when present in soils and ground water.[24] DNT is often found as an impurity in TNT samples[25] – it is used as a starting material to manufacture TNT – and DNT is an environmental contaminant in its own right.[26] The ability to detect TNT is also a security concern due to its potential use by terrorists. The need to detect these species is therefore imperative, and a simple inexpensive sensor to identify and quantify these species in the field would be highly regarded.[27]

The electrochemical behaviour of TNT and DNT has been relatively well studied in protic solvents, where the number of reduction peaks in the voltammograms correspond to the number of nitro groups on the aromatic ring, i.e. three for TNT, and two for DNT.[28-33] The nitro groups are irreversibly reduced to hydroxylamines or amines, depending upon the pH of the solvent.[28-33] A general reaction mechanism for the first reduction peak in aqueous (acidic) solutions is described by Vu et al.:[34]

$$\mathbf{\emptyset\text{–}NO_2 + 2}\boldsymbol{e}^{-}\mathbf{+ 2H^+ \rightarrow \emptyset\text{–}NO + H_2O} \quad (1)$$

$$\mathbf{\emptyset\text{–}NO + 2}\boldsymbol{e}^{-}\mathbf{+ 2H^+ \rightarrow \emptyset\text{–}NHOH} \quad (2)$$

$$\mathbf{\emptyset\text{–}NHOH + 2}\boldsymbol{e}^{-}\mathbf{+ 2H^+ \rightarrow \emptyset\text{–}NH_2 + H_2O} \quad (3)$$

In aprotic RTILs, the number of reduction peaks are the same,[35-41] however, the first reduction peak is believed to proceed via a one-electron reduction step to the radical anion for both TNT[39] and DNT[40] (see equation 4), followed by dimerization of the radical anion and/or proton abstraction at high concentrations.[39-40]

$$\mathbf{\emptyset\text{–}NO_2 +}\ \boldsymbol{e}^{-} \rightleftharpoons \mathbf{\emptyset\text{–}NO_2}^{*-} \quad (4)$$

From a sensing perspective, it is usually the current of the first reduction peak that will be used for quantification, and this is likely to be affected if moisture is present in the RTIL, resulting in protons partaking in follow-up chemical reactions. Air environments may also affect the currents for the detection step, especially if the reduction peak occurs at similar potentials to oxygen reduction. We have therefore investigated the effect of oxygen, air and moisture on the electrochemical responses of TNT and DNT reduction in an ionic liquid, using cyclic voltammetry (CV) and square wave voltammetry (SWV). Various other nitroaromatic compounds have also been examined to determine if the compounds can be selectively

determined in a mixture, and finally a mixture of TNT and DNT is examined to determine if these two compounds can be simultaneously detected and quantified. This work will be useful for understanding the effects of environmental factors and interfering species on the sensing of explosive analytes in RTILs.

Experimental

Chemicals and reagents

The RTIL trihexyltetradecylphosphonium bis(trifluoromethylsulfonyl)imide ($[P_{14,6,6,6}][NTf_2]$) was kindly donated by Prof Chris Hardacre (now at the University of Manchester, UK) and was used as received, without any further purification. The nitroaromatic compounds 2,4-dinitrotoulene (2,4-DNT), 2,6-dinitrotoulene (2,6-DNT), 1,3-dinitrobenzene (1,3-DNB) and 2,4,6-Trinitrotoluene (2,4,6-TNT) were purchased from Cerilliant Corporation (Round Rock, Texas, USA) as solutions of 1000 µg/mL in acetonitrile. Unless explicitly stated, the mentioning of DNT in the text refers to the more common isomer, 2,4-DNT. 1,3,5-Trinitrobenzene (1,3,5-TNB) was a solid sample from Sigma-Aldrich (Missouri, USA), and Musk Xylene (MX) was from Sigma-Aldrich as a solution of 100 µg/mL in acetonitrile. Ferrocene (Fc, $Fe(C_5H_5)_2$, 98 %) and tetra-*N*-butylammonium perchlorate (TBAP, 98 %) were from Sigma-Aldrich. Acetonitrile (MeCN, 99.8 %), methanol (99.9 %), and acetone (99.9 %) were from Sigma-Aldrich, and ultrapure water (resistance = 18.2 MΩ·cm, prepared by an ultrapure laboratory water purification system from Millipore Pty Ltd., North Ryde, NSW, Australia) were used for rinsing the electrodes before and after use. Oxygen (O_2, >99.5 %) and nitrogen gas (N_2, >99.99 %), purchased from BOC gas (Welshpool, WA, Australia) were mixed (based on relative flow rates, as described in previous work)[42] to produce the different O_2 concentration, and for N_2-purging of the electrochemical cell.

Sample preparation

For samples that were prepared from acetonitrile solutions, a suitable aliquot (~25 µL) of the stock solution was precisely gravimetrically measured into a clean 1 mL centrifuge vial, followed by overnight evaporation of the acetonitrile under vacuum. The moles of the analyte available in the vial was estimated based on the mass and concentration of the stock solution added and the density of the solvent (MeCN). The RTIL was then added at an appropriate volume (gravimetrically measured) to make up the required concentrations. For the 2,4-DNB solid sample, a 2000 µg/mL acetonitrile solution was first made up, and the RTIL samples were then prepared according to the same procedure. For the DNT-TNT mixed sample at 50:50 molar ratio, appropriate aliquots of the two respective stock solution was precisely measured first and then also prepared according to the above procedure. For reference potential calibration, ferrocene (Fc) was added at the end of the experiment using a 0.5–20 µL plastic micro-pipette tip (Eppendorf, Hamburg, Germany). A small amount of solid ferrocene was dropped into the nitroaromatic/RTIL solution, before being gently stirred with the pipette tip to aid dissolution. The cyclic voltammograms were then shifted so that the midpoint of the ferrocene/ferrocenium redox couple was at 0 V. We note that ferrocene was not added in-situ for the experiments performed in oxygen, air, or different humidity environments. This is because the presence of three electroactive species in the RTIL (i.e. TNT/DNT, oxygen, and ferrocene) is too complicated and may give rise to additional chemical reactions. Previous literature reports have indicated the non-innocent nature of analyte species even when only two species were present in the RTIL.[43-44]

Instrumental

Electrochemical experiments were conducted using a PGSTAT101 Autolab potentiostat (Eco Chemie, Netherlands), interfaced to a PC with NOVA software. The electrochemical cell was placed inside a custom-made

aluminum Faraday cage in a fume cupboard at standard laboratory temperature (294 ± 1 K). A scan rate of 100 mVs^{-1} was typically employed for cyclic voltammetry (CV) experiments. Optimised square wave voltammetry (SWV) parameters were: an amplitude of 20 mV and frequency of 50 Hz. A conventional two-electrode arrangement was employed, with a homemade gold microelectrode (radius 13 μm) as the working electrode, with a 0.5 mm diameter silver wire (Sigma-Aldrich) as a combined counter electrode and (quasi-)reference electrode. The microdisk electrode was polished on soft lapping pads (Buehler, Lake Bluff, IL) with alumina powder of decreasing size (3, 1, and 0.5 μm, Kemet, NSW, Australia).The working electrode radius was calibrated electrochemically using 3 mM ferrocene in acetonitrile with 0.1 M TBAP and adopting a value for the diffusion coefficient of 2.3×10^{-9} m^2 s^{-1} at 298 K.[45] A reservoir at the tip of the electrode was created (with a cut segment of a 2–200 μL micropipette tip), into which microliter quantities (ca. 20 μL) of the RTIL/analyte solution could be placed. The electrodes were housed inside a glass "T-cell",[46] RTIL/analyte sample was purged under high vacuum (Edwards high vacuum pump, Model ES 50) to remove oxygen and dissolved atmospheric moisture for > 1 hour, before introducing the N_2-gas (at 480 sccm).

For the different humidity experiments, measurements were conducted in dry air (passed through a regular air scrubber/filtration system supplied by the laboratory building), ambient air (measured to be at ~34% RH) using a RH/Temperature meter (20–95 % RH, SPER Scientific, RH/Temperature Pen – 800012, Arizona, USA). The air was drawn through the cell at a constant flow rate (ca. 300 sccm) by connecting the cell to the vacuum line of the lab. Moist air and moist N_2 (both ~86% RH) was generated by vigorously bubbling the gas through a container of water before feeding it into the cell.

Safety Considerations

Nitroaromatic compounds are generally classified as hazardous substances and should be handled by trained individuals inside a chemical fume hood at all times. It is essential to store and work with tiny amounts of material, where possible. A lab coat, enclosed shoes, safety goggles, and Viton gloves should be worn, and hands should be properly washed with soapy water after handling. In particular, TNT is classified as a high explosive, which can become reactive under high temperatures and/or pressures, and may detonate when subjected to shock or friction, and can also react with reducing agents. TNT should be stored separately, well away from initiators, combustibles, oxidising materials, and be kept away from potential physical damage and sources of heat. The hazardous waste generated should be stored in a separate container and transferred for disposal within 90 days.

Results and Discussion

Voltammetry of TNT and DNT in the presence of oxygen

To study the effect of oxygen on the voltammetry of the explosive compounds TNT and DNT, different concentrations of oxygen were introduced into the atmosphere of the cell containing the sample. The RTIL $[P_{14,6,6,6}][NTf_2]$ was chosen as the solvent, since it was previously shown that the oxygen reduction process in this RTIL has slow kinetics, resulting in the oxygen reduction peak occurring at more negative potentials than the TNT first reduction peak.[47] For these experiments, a concentration of ~3 mM TNT or DNT was used, and the concentration of oxygen was varied at 0, 5, 10, and 20 % vol. O_2 (estimated to be 0, 0.38, 0.75, and 1.5 mM, based on a solubility of 7.5 mM for oxygen reported in this RTIL).[20] The highest concentration (20 % O_2) most closely resembles the amount of oxygen in ambient environments (ca. 21 % O_2 at sea level). Hence, it is important to study its effect on the voltammetry of the explosive compounds if these compounds are to be detected in the field.

Figure 1 shows CVs for the reduction of TNT and DNT, respectively: where (a and c) shows peak 1 only, and (b and d) shows peaks 1 and 2, in the presence of 0 (blue), 5 (purple), 10 (green) and 20 (red) % vol. O_2. In the absence of oxygen (blue line), the CV closely resembles a reversible redox process, consistent with that reported previously at these concentrations (see equation 4).[39-40] As oxygen is introduced up to 20 % vol., the reduction peak current for TNT increases only slightly (by ~20 %, Figure 1a), while the reverse peak also decreases, showing a small but noticeable effect from oxygen on the voltammetry. However, the second reduction peak of TNT is significantly more affected by the presence of oxygen (Figure 1b), with the addition of 20 % O_2 giving rise to ca. 7 times the current response in the absence of oxygen. At this potential, the current is a combination of both TNT reduction and oxygen reduction into a single broad peak. Oxygen reduces to superoxide in RTILs according to equation 5, and the shape of the reductive voltammetry is similar to that reported previously for oxygen in $[P_{14,6,6,6}][NTf_2]$.[48]

$$\mathbf{O_2} + \boldsymbol{e}^- \rightleftharpoons \mathbf{O_2}^{*-} \qquad (5)$$

The reverse peak shape in Figure 1b is quite different in the presence of oxygen, with the absence of a clear oxidation peak. As the concentration of oxygen is increased, this oxidation peak becomes smaller, suggesting a possible reaction of the electrogenerated superoxide with TNT or its reduction products. This is not unexpected, since superoxide is known to be a strong base capable of deprotonating even weak acids in solution[49]; TNT has a weakly acidic proton on the methyl group attached to the aromatic ring. Alternatively, superoxide can also abstract a proton directly from the phosphonium cation of the RTIL ($[P_{14,6,6,6}]^+$), as reported by Li et al.[50] for oxygen reduction in a similar RTIL with the same cation.

For DNT, peak 1 is substantially more affected by the presence of oxygen (Figure 1c) compared to TNT, due to the more negative reduction potential for DNT compared to TNT (the reduction potentials will be discussed in more detail later). Even with the addition of only 5 % O_2, the current of the DNT reduction peak is more than double that observed in the absence of oxygen; at 20 % O_2, it is almost 5 times that expected. At these potentials, it is likely that the current response is a superposition of both DNT reduction and oxygen reduction contributions. There is also an additional oxidation peak present at ca. +0.2 V on the reverse sweep after scanning over peak 1, which gets larger as the amount of oxygen is increased. This is likely due to the oxidation of an electrogenerated product from the reduction step. As the potential is widened further to include the second reduction of DNT

(Figure 1d), the current of peak 2 also increases. This second reduction peak becomes very broad and drawn out, likely because superoxide can also be further reduced to peroxide at these potentials,[49] which could then interact with the other species present, and the reduction process becomes quite complicated at these potentials.

The insets to Figures 1b and 1d show the equivalent SWVs for the first two reduction processes of TNT and DNT in the absence and presence of different oxygen concentrations. The first reduction peak of TNT is relatively unaffected by O_2 (Figure 1b inset, Peak 1), with only a 6 % increase in current, suggesting that square wave voltammetry is a more favourable technique compared to CV (22 % increase) for quantifying TNT in an oxygenated environment. In contrast, due to DNT reduction occurring at similar potentials to oxygen reduction, the SWV current for peak 1 of DNT is strongly affected by oxygen (Figure 1d inset) and cannot be reliably quantified in an oxygenated environment. This suggests that oxygen needs to be removed from the electrolyte for accurate quantification of DNT.

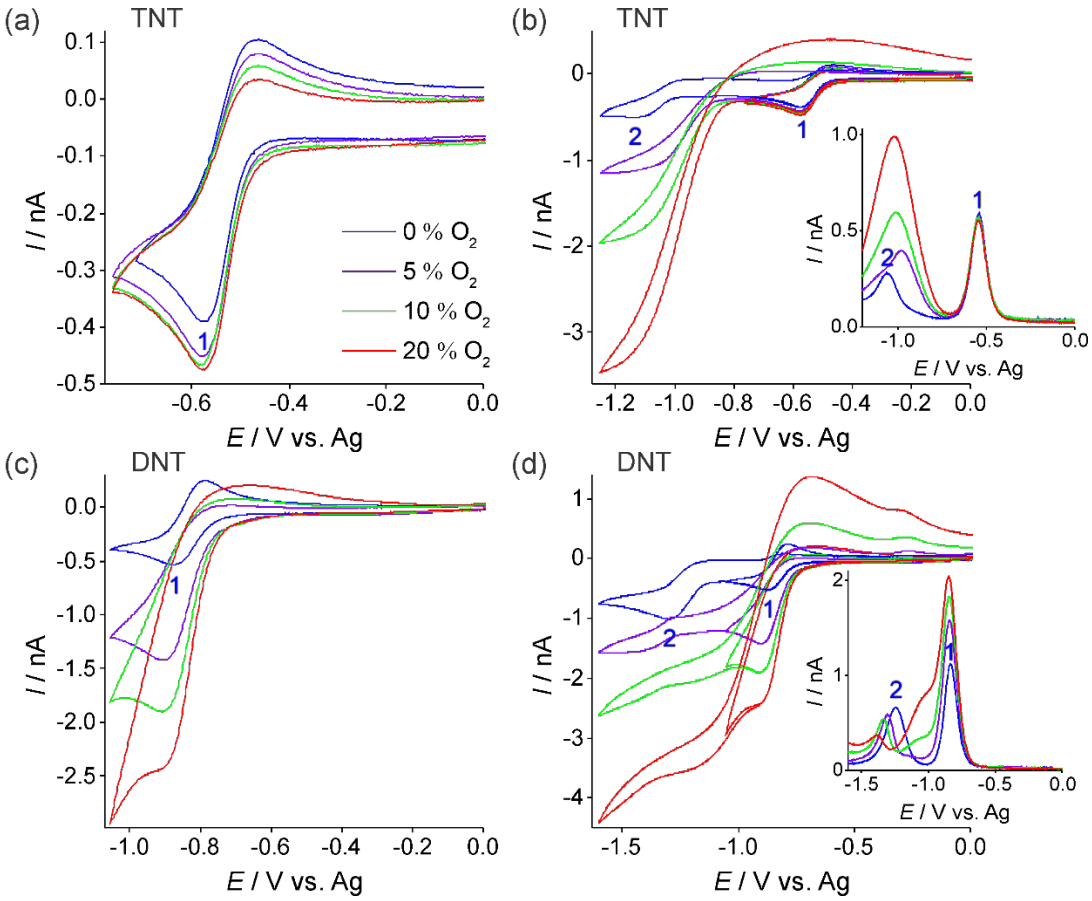

Figure 1. CVs at 100 mVs^{-1} showing the addition of different concentrations of oxygen (0, 5, 10 and 20 % vol.) for: (a) TNT peak 1, (b) TNT peaks 1 and 2, (c) DNT peak 1, and (d) DNT peaks 1 and 2, on a gold microdisk electrode (diameter 26 µm) in [$P_{14,6,6,6}$][NTf_2]. The inset figures show the equivalent square wave voltammograms (amplitude = 20 mV, frequency = 50 Hz, and υ = 100 mV s^{-1}) under the same conditions.

Voltammetry of TNT and DNT in the presence of ambient air and moisture

The effect of moisture and air on the voltammetry was also studied. Figure 2 shows CVs for the reduction of (a) TNT and (b) DNT in a range of environments: dry nitrogen, dry air, ambient air (~34 % relative humidity, RH), moist air (~86 % RH) and moist nitrogen (~86 % RH) in [$P_{14,6,6,6}$][NTf_2]. As can clearly be seen, the voltammetry of both TNT and DNT is significantly affected by the different environments.

For TNT (Figure 2a), an additional pre-peak appears before the first TNT reduction peak due to the presence of water – it is not present in either the dry N_2 or dry air CVs (blue and purple lines). This pre-peak current is significant compared to the analyte peak, which undesirably affects the analytical signals. The SWV (Figure 2a, inset) also shows that the peak 1 current is increased in the presence of moisture, in addition to the presence of the large and broad pre-peak. This pre-peak appears to be suppressed in the presence of oxygen, since the CV in moist N_2 gave a larger pre-peak compared to the CV in moist air. If TNT is to be sensed in moist atmospheric conditions, where drying of the sample is not possible, this behaviour needs to be taken into account. The results in Figure 1 show that for SWVs, peak 1 current of TNT is relatively unaffected by oxygen concentrations up to 20% O_2. However, in the "dry air" sample in Figure 2a (purple), the SWV peak 1 current of TNT is appreciably higher (a 13 % increase). This hints that some moisture is still present in the dried lab-reticulated air, which is below the measurable humidity level of the meter used (20 % RH).

The CV peak current for DNT is also affected by moisture – blue vs orange lines in Figure 2b correspond to dry vs moist N_2 environments), with a ca. 40 % increase in current. However, for DNT, oxygenated environments have more of a dramatic effect on the current – an approximate 17-fold increase in current is observed in moist air (red) compared to dry N_2 (blue). 8.6 times and 9.8 times increased currents are also observed in dry air (purple) and ambient air (green), respectively. For DNT, it appears that oxygen has a much greater effect on the sensing response compared to moisture. Overall, the results in Figure 2 show that for both TNT and DNT, the sample needs to be dried before accurate quantification of these species can be reliably performed.

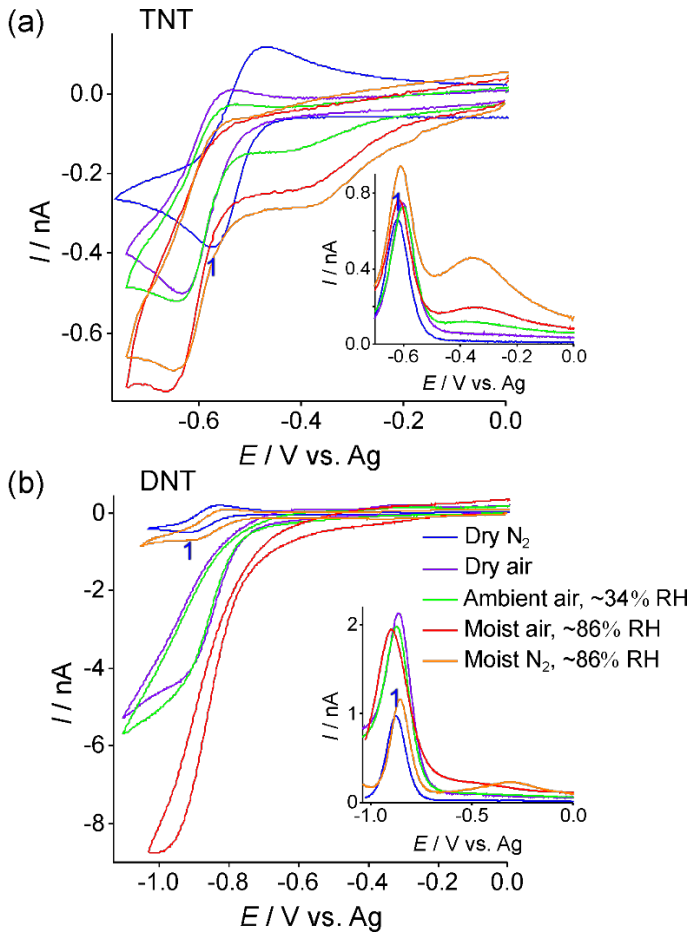

Figure 2. CVs and (inset) SWVs in $[P_{14,6,6,6}][NTf_2]$ on a gold microdisk electrode (diameter 26 μm) for: (a) TNT peak 1, and (b) DNT peak 1, in the absence and presence of moisture (different relative humidities – RH) in air or nitrogen.

Voltammetry of Other Nitroaromatic Explosive Compounds

In order to study the possible influence of other nitroaromatic based compounds on the detection of TNT and DNT in mixed environments, the voltammetry of some related nitroaromatic compounds was studied. Figure 3 shows the chemical structures of the six compounds studied – some with two nitro groups, and some with three nitro groups present on the aromatic ring. The compounds were studied individually to observe their uncomplicated voltammetric behaviour in solution, and report their relative reduction peak potentials.

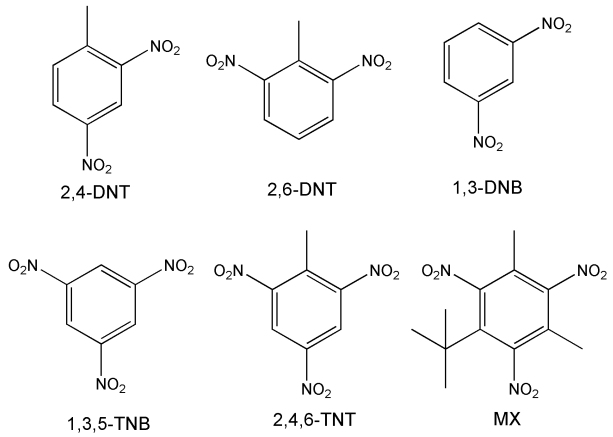

Figure 3. Chemical structures of the explosive compounds used in this study, and their abbreviations.

Figure 4 shows typical CVs (100 mVs^{-1}) for the reduction of the six nitroaromatic compounds on a Au microdisk electrode in $[P_{14,6,6,6}][NTf_2]$ vs the ferrocene/ferrocenium redox couple. The compounds with two nitro groups display two obvious reduction peaks, labelled 1 and 2, and the compounds with three nitro groups display three reduction peaks, labelled 1, 2 and 3, with each peak corresponding to the reduction of one nitro group. It is clear that the shapes of the voltammograms are affected by the constituents and positions on the aromatic ring. For the dinitroaromatics, changing one nitro group from the -4 to -6 position (Figures 4b and 4c) results in a larger reduction current for peak 2 (suggesting a different reduction mechanism, or larger electron count for this process), although the current for peak 1 is largely unchanged. However, when the methyl group is removed from the aromatic ring in 1,3-DNB, the doubly-reduced species appears to be much more stable on the voltammetric timescale, such that chemically reversible voltammetry is observed for peak 2 (Figure 4a). This is consistent with the deprotonation mechanism suggested earlier for 2,4-DNT;[51] the absence of the methyl group in 1,3-DNB means there is no readily available proton to undergo deprotonation, and the reduction product is thus more stable.

For the trinitroaromatics, interestingly, peak 1 is chemically irreversible for 1,3,5-TNB (Figure 4d) at 100 mVs^{-1}. This is consistent with that reported by Gallardo et al.,[52] who studied the electrochemical reduction of 1,3,5-TNB in acetonitrile. They assigned this behaviour to the dimerisation of the radical anion, which was much more readily formed compared to the mono- and di-nitro benzene compounds. In their work, the resulting follow-up product for 1,3,5-TNB reduction was oxidised on the anodic sweep, which is consistent with our results in Figure 4d. For the reduction of 2,4,6-TNT, peak 1 appears to be chemically reversible under these conditions, but peaks 2 and 3 show some degree of irreversibility, consistent with that reported previously.[39] Musk Xylene (MX) was also studied (Figure 4f), due to its use as a perfume fixative; is still used in some cosmetics and fragrances, with the possibility to cause false positives on a person being swabbed for explosive residue. Peak 1 for MX is mostly reversible, with peaks 2 and 3 having slower kinetics. The electrogenerated reduction products from peaks 2 and 3

are oxidised on the anodic scan.

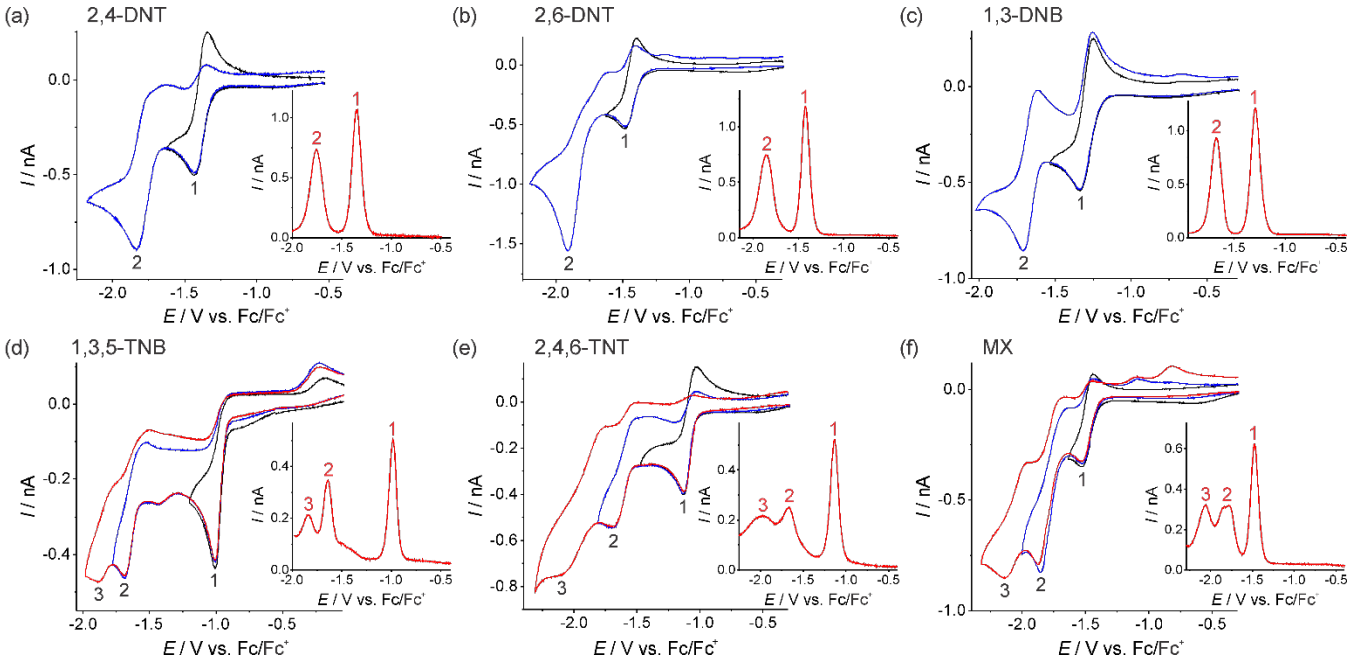

Figure 4. Cyclic voltammograms (scan rate 100 mVs^{-1}) and (inset) square-wave voltammograms (amplitude = 20 mV, frequency = 50 Hz, and υ = 100 mV s^{-1}) for (a) 1,3-DNB, (b) 2,4-DNT, (c) 2,6-DNT, (d) 1,3,5-TNB, (e) 2,4,6-TNT, and (f) MX (ca. 3 mM) on a gold microelectrode (diameter 26 μm) in [$P_{14,6,6,6}$][NTf_2].

Table 1 shows the peak-to-peak separations, ΔE_p, for peak 1, along with the potentials, E_{Peak}, for peaks 1, 2 and 3. The peak-to-peak separations are relatively similar (81–-95 mV) for all compounds, suggesting that the electrochemical kinetics for the first reduction process is not significantly affected by changing the substituents on the aromatic ring. We note it was not possible to measure ΔE_p for 1,3,5-TNB due to the lack of a reverse peak.

Table 1. Summary of the peak-to-peak separation of peak 1 (from CV), and the peak potentials for peaks 1, 2 and 3 from CV and SWV for different nitroaromatic compounds in [$P_{14,6,6,6}$][NTf_2].

Species, X	[X] / mM	ΔE_{Peak1} / mV	$E_{Peak1,CV}$ / V	$E_{Peak2,CV}$ / V	$E_{Peak3,CV}$ / V	$E_{Peak1,SWV}$ / V	$E_{Peak2,SWV}$ / V	$E_{Peak2,SWV}$ / V
1,3-DNB	2.89	81	-1.34	-1.72	-	-1.29	-1.68	-
2,4-DNT	2.97	81	-1.43	-1.84	-	-1.35	-1.76	-
2,6-DNT	2.98	85	-1.49	-1.91	-	-1.42	-1.85	-
1,3,5-TNB	2.93	n/a^A	-1.01	-1.69	-1.89	-0.98	-1.64	-1.84
2,4,6-TNT	3.04	95	-1.13	-1.69	-2.09	-1.13	-1.67	-1.98
2,4,6-MX	2.70	85	-1.53	-1.85	-2.14	-1.48	-1.78	-2.06

^{A} = no clear oxidation peak observed. All potentials are reported vs the ferrocene/ferrocenium redox couple.

The peak potentials, E_{Peak}, can be used as an indication of whether the compounds can be selectively determined in a mixed environment. There is a relatively large variation in reduction peak potentials for peak 1 in the six compounds (-1.01 V to -1.53 V, see Table 1), suggesting that selective determination may be possible. For the dinitroaromatics, simply by changing one nitro group from the -4 to -6 position on DNT, a shift of ca. 60 mV is observed. When the methyl group is removed from the ring, the 1,3-DNB is reduced more easily (by ca. 90 mV compared to 2,4-DNT). Since alkyl substituents attached to a ring are typically electron donating, it is reasonable that 2,4-DNT will reduce at a more negative potential than 1,3-DNB due to the higher electron density localised on the aromatic ring. Similarly, for the trinitroaromatics, the reduction follows the order 1,3,5-TNB < 2,4,6-TNT < MX, with musk xylene being the hardest to reduce due to the presence of several alkyl substituents. Finally, it is

noted that 2,4,6-TNT is much easier to reduce than 2,4-DNT (by ca. 300 mV) since it has one more nitro group (electron withdrawing) on the aromatic ring. This suggests that selective determination is indeed possible by applying different potentials. Importantly, the reduction potential for musk xylene is 400 mV more negative than for 2,4,6-TNT, making it unlikely that perfumes/cosmetics that contain this substance will give false positives for an electrochemical sensor that is detecting 2,4,6-TNT.

The insets to Figure 4 show SWV measured for the six compounds in $[P_{14,6,6,6}][NTf_2]$ on a microdisk electrode. All peaks appear to be sharp and well defined for the six compounds studied. In particular, peak 1 for 1,3,5-TNB and 2,4,6-TNT are well separated from peaks 2 and 3, making extraction of currents from peak 1 very simple. There is a slight shoulder before peak 2 for 1,3,5-TNB, consistent with the additional small bump observed in the CV, and is likely to be due to reduction of a product from the irreversible first reduction. The SWV background currents are relatively flat compared to CV due to the method of sampling that minimises non-Faradaic processes. Overall, SWV appears to be a highly suitable technique for 'fingerprinting' of compounds in a mixed environment due to the well-defined reduction peak potentials that are characteristic of each compound.

Voltammetry of mixed sample of TNT and DNT

In a real forensic sample of explosives, e.g. those found at crime scenes or in the environment, it is possible that there may be a mixture of compounds present. An obvious mixture to study is therefore TNT and DNT, since DNT is often used in the synthesis of TNT. In this study both species were dissolved into the RTIL at equal molar concentration, to observe the voltammetry in a mixed sample. Figure 5 shows: (a) CV and (b) SWV for the reduction of a 1:1 mixture of DNT and TNT in $[P_{14,6,6,6}][NTf_2]$; the red line shows the reduction of 3 mM TNT alone, the blue line shows the reduction of 3 mM DNT alone, and the green line shows the reduction of a mixture of 3 mM TNT + 3 mM DNT. The CVs have also been reversed after each reduction peak, to show the reversibility of the peaks, and the voltammetry has been shifted to the ferrocene/ferrocenium redox couple, as described in the experimental section.

CV for the mixed sample (Figure 5a, green line) shows three distinct reduction peaks, not the 5 as expected from a mixture of these two compounds. This is since peaks 2 and 3 for TNT reduction, and peak 2 for DNT reduction, are superimposed into one broad peak, with an overall peak potential of –1.83 V vs Fc/Fc^+. These overlapping processes are therefore very difficult to resolve from one another in the mixture; and is also the case even in the SWV (Figure 5b) – where many of the background processes are removed. However, importantly, the first reduction peaks (used as the analytical signal) for TNT and DNT are well separated, and easy to identify based on the reduction potentials. Compared to the pure TNT sample, peak 1 current for TNT is only minimally affected by the presence of DNT using CV, and is almost identical using SWV. Overall, the results show that there is no significant interaction between the two analytes present in the same sample. Additionally, because of the large separation between peaks 1 and 2 for TNT, the SWV current for peak 1 for DNT is almost exactly the same as the pure DNT sample. This important observation means that it should be possible to identify (based on the reduction potential) and accurately quantify (based on the peak current) both TNT and DNT in a mixture using the square wave voltammetry technique.

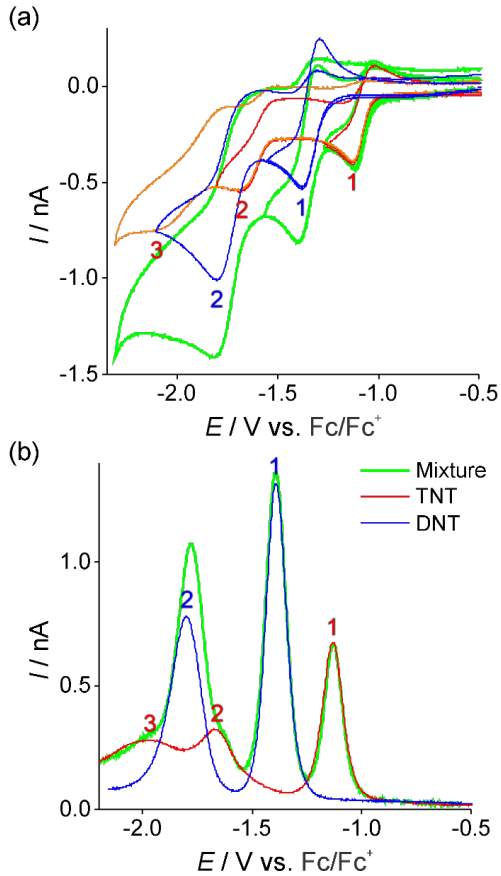

Figure 5. (a) CVs and (b) SWVs for: 3 mM TNT reduction (red line), 3 mM DNT reduction (blue line) and a mixture of 3 mM TNT + 3 mM DNT (green line) in $[P_{14,6,6,6}][NTf_2]$ on a gold microdisk electrode (diameter 26 µm). CVs in (a) are reversed after the individual peaks to show the reversibility of the reduction processes.

Conclusions

Cyclic voltammetry and square wave voltammetry for TNT and DNT reduction in a range of mixed environments has been studied. It was shown that oxygen does not have a significant influence on the analyte current for TNT (first peak), but significantly affects the current for DNT. Therefore, samples would need to be degassed or flushed with an electrochemically inert gas (e.g. N_2 or Ar) before the accurate quantification of DNT in the environment. Water was found to have a very significant effect on the sensing signals for both TNT and DNT, requiring either drying of the sample before measurement, or calibration of the current signals in different humidity environments. The behaviour of both TNT and DNT was also compared to other di- and tri-nitroaromatic species, suggesting the ability to identify the compound present based on the different peak shapes and reduction potentials in the RTIL solvent. This is evident in a mixture of TNT and DNT, where each of the compounds could be separately identified and quantified using square wave voltammetry. This enables the identification and quantification of both compounds in a mixed analyte sample.

Conflicts of Interest

The authors declare no conflicts of interest.

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