Talanta 88 (2012) 743–748

Contents lists available at SciVerse ScienceDirect

Talanta

journal homepage: www.elsevier.com/locate/talanta

Short communication

Chemiluminescence detection of 1,3,5-trinitro-1,3,5-triazacyclohexane (RDX) and related nitramine explosives

David N. Donaldson[a], Neil W. Barnett[a], Kent M. Agg[a], Duncan Graham[b], Claire E. Lenehan[c,d], Chad Prior[d,e], Kieran F. Lim[a], Paul S. Francis[a,*]

[a] *School of Life and Environmental Sciences, Deakin University, Waurn Ponds, Victoria 3216, Australia*
[b] *Department of Pure and Applied Chemistry, University of Strathclyde, Glasgow, UK*
[c] *School of Chemical and Physical Sciences, Flinders University, Adelaide, South Australia 5001, Australia*
[d] *Centre of Expertise in Energetic Materials (CEEM), Australia*
[e] *Weapons Systems Division, Defence Science and Technology Organisation (DSTO), Edinburgh, SA 5111, Australia*

ARTICLE INFO

Article history:
Received 29 September 2011
Received in revised form
17 November 2011
Accepted 17 November 2011
Available online 25 November 2011

Keywords:
Cyclotrimethylenetrinitramine
Chemiluminescence detection
Ruthenium complexes
Nitramine explosive
Flow injection analysis

ABSTRACT

A simple controlled chemical reduction of 1,3,5-trinitro-1,3,5-triazacyclohexane (RDX) and related nitramine compounds with zinc amalgam generates species that elicit intense chemiluminescence with tris(2,2′-bipyridine)ruthenium(III), which extends this widely utilised chemiluminescence reagent to a new class of analyte and presents a sound chemical basis for a screening test for nitramine high explosives. Examination of the chemiluminescence profiles under stopped-flow conditions revealed contributions from multiple transient species formed in the initial reduction step.

1. Introduction

Rapid at-scene detection of explosives such as 1,3,5-trinitro-1,3,5-triazacyclohexane (RDX; Fig. 1) is of paramount importance in the fight against organised crime and terrorism [1–3], but practical and cost-effective equipment currently available to field personnel to conduct screening tests is very limited. Microfluidics is seen as a promising technique to address this issue [4,5] and there is therefore an urgent need for new detection systems suitable for miniaturised flow-analytical devices. Chemiluminescence is an attractive mode of detection for microfluidics because of its inherent sensitivity and instrumental simplicity [6–8], but it is limited by the relatively small number of effective reagents [9]. Amongst these, tris(2,2′-bipyridine)ruthenium(III) ($Ru(bipy)_3^{3+}$) has been one of the most widely applied [8,10–14]. Preliminary chemical or electrochemical oxidation of $Ru(bipy)_3^{2+}$ and subsequent reduction of $Ru(bipy)_3^{3+}$ by a suitable analyte (or analyte oxidation product [15]) forms the $[Ru(bipy)_3^{2+}]^*$ species responsible for the characteristic orange luminescence from this reaction [13,16]. The radiative relaxation to the ground electronic state regenerates $Ru(bipy)_3^{2+}$, which enables repeated use of the reagent if immobilised in the detection flow-cell or electrode surface [11,12].

Aliphatic tertiary amines elicit the greatest emission with this reagent, and consequently the vast majority of analytical applications focus on the detection of compounds containing this functional group, or biomolecules labelled with $Ru(bipy)_3^{2+}$ using tripropylamine as a co-reactant [11,17,18]. However, some innovative approaches to extend $Ru(bipy)_3^{2+}$ chemiluminescence detection to new classes of analytes (such as primary or aromatic amines, nitrosamines and carboxylic acids) have emerged [19–32], including photochemical reactions, and derivatisation to add or form tertiary amines (Table 1).

Nitramine compounds such as the high explosive RDX have not previously been detected with $Ru(bipy)_3^{2+}$ chemiluminescence, but McHugh et al. have demonstrated controlled reductions of RDX to products that included hydrazine and tertiary amines [33], which reveals a pathway to potentially utilise $Ru(bipy)_3^{2+}$ chemiluminescence detection. Moreover, Woltman et al. [34] have quantified nitroaromatic and nitramine explosives (including RDX) by electrochemical reduction to form hydroxylamines and nitrosamines that reacted with $Ru(bipy)_3^{3+}$ to produce $Ru(bipy)_3^{2+}$, which they

---

* Corresponding author at: Deakin University, Locked Bag 20000, Geelong, Victoria 3220, Australia. Tel.: +61 3 5227 1294; fax: +61 3 5227 1040.
E-mail address: paul.francis@deakin.edu.au (P.S. Francis).

0039-9140/$ – see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.talanta.2011.11.051

Table 1

Derivatisation/degradation procedures that extend $Ru(bipy)_3^{2+}$ chemiluminescence to the detection of analytes that otherwise elicit no (or relatively low) native response.

Analyte	Instrument (mode of detection)	Approach	Proposed or identified product(s)	Limits of detection	Ref.
Amino acids	HPLC (ECL)	Off-line derivatisation with dansyl chloride (60 min deriv.; 40–60 min sep.)	Dansyl amino acids	1×10^{-7} M	[19]
Amino acids	HPLC (CL)	On-line oxidation with periodate and UV irradiation (10–15 min sep.)	Oxalate	5×10^{-8} M to 2×10^{-6} M	[20]
Aromatic and branched-chain amino acids	FIA/HPLC (ECL)	Off-line cyclisation using DVS (15 min deriv.; 40 min sep.)	1,4-Thiazane-1,1-dioxide derivatives (tertiary amines)	4×10^{-9} M to 8×10^{-7} M	[21]
Primary amines	HPLC (ECL)	Off-line cyclisation using DVS (15 min deriv.; 12 min sep.)	1,4-Thiazane-1,1-dioxide derivatives (tertiary amines)	1×10^{-7} M (3-aminopentane), 3×10^{-6} M (propylamine)	[22]
Enantiomers of chiral secondary amines	Chiral HPLC (CL)	On-line derivatisation with acrylonitrile (30 min sep.)	Tertiary amines	Not stated	[23]
Monoethanolamine and diethanolamine	FIA/HPLC (CL)	On-line derivatisation with epichlorohydrin (7.5 min deriv.; 30 min sep.)	Tertiary amines	1×10^{-6} M	[24]
Aromatic amines	FIA/HPLC (CL)	On-line UV irradiation (30 min sep.)	Various substituted amines	1×10^{-7} M to 1×10^{-6} M	[25]
Aliphatic and aromatic amines	HPLC (ECL)	Off-line derivatisation using diketene (90 min deriv. aromatic, 5 min deriv. aliphatic; 30 min sep.)	Acetoacetylamides	5×10^{-7} M	[26]
Penicillamine and ephedrine	SIA (CL[a])	Off-line derivatisation with acetaldehydes (30 min deriv.; 20 min sep.)	N-substituted hemiaminals	7×10^{-7} M and 2×10^{-7} M	[27]
Nitrosamines	FIA/HPLC[b] (CL[a])	On-line UV irradiation inducing N-NO cleavage (25 min sep.)	Secondary amine	4×10^{-10} M to 8×10^{-9} M[c]	[28]
N–Methylcarbamates	HPLC[b] (CL[a])	Post-column irradiation by UV light (18 min sep.)	Methylamine	2×10^{-11} M to 2×10^{-10} M	[29]
Carboxylic acids	HPLC (ECL)	Off-line derivatisation with IDHPIA (45 min deriv.; 80 min sep.)	Tertiary amine	5×10^{-11} M (myristic acid), 6×10^{-11} M (phenylbutylic acid)	[30]
Carbonyl compounds	FIA/HPLC (ECL)	Off-line derivatization with methylmalonic acid (20 min deriv.; 10 min sep.)	Cyclic dilactone derivatives	2×10^{-9} M to 2×10^{-7} M	[31]
Aromatic compounds	HPLC (CL)	On-line UV irradiation (10–50 min sep.)	Oxalic acid	4×10^{-8} M (ECGC), 6×10^{-8} M (epicatechin)	[32]
Nitramines	FIA (CL)	Off-line Zn–amalgam reduction with ultrasonication (12 min)	Substituted amine species	1×10^{-8} M (RDX)	This study

Abbreviations: CL: chemiluminescence; deriv. = derivatisation; DVS: divinyl sulfone; ECGC = epigallocatechin gallate; ECL: electrochemiluminescence (in some of the above cases more appropriately described as prior electrochemical generation of the reagent for chemiluminescence); FIA: flow-injection analysis; HPLC: high performance liquid chromatography; IDHPIA: 3-isobutyl-9,10-dimethoxy-1,3,4,6,7,11b-hexahydro-2H-pyrido[2,1-a]isoquinolin-2-ylamine; sep. = chromatographic separation; UV = ultraviolet.

[a] Reagent oxidised using peroxydisulfate with UV irradiation.

[b] Incorporating preliminary solid phase extraction.

[c] Limits of detection shown were obtained without the preconcentration step.

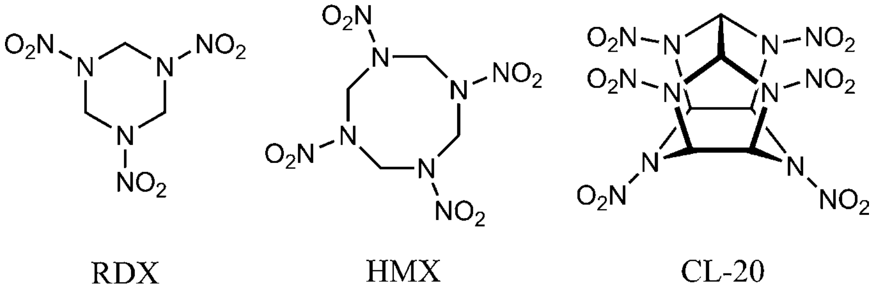

Fig. 1. Nitramine explosives: 1,3,5-trinitro-1,3,5-triazacyclohexane (RDX), octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX) and 2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane (CL-20).

detected by laser-induced photoluminescence. We report a new approach for the detection of RDX exploiting the selective formation of chemical-reduction intermediates that elicit an intense chemiluminescence response with $Ru(bipy)_3{}^{3+}$, hereby demonstrating for the first time, the extension of this widely utilised reagent to the detection of nitramine compounds.

2. Experimental

2.1. Flow injection analysis manifold

The flow injection system was constructed from a peristaltic pump, a two-position six-port valve with a 70 μL injection loop, and flow cell comprising a coil of PTFE-PFA tubing (0.8 mm i.d.) positioned flush against an extended range photomultiplier tube (PMT, model 9828SB, ET Enterprises), as previously described [35]. The $Ru(bipy)_3{}^{3+}$ reagent was injected into a carrier stream (5% H_2SO_4 in ethanol or acetonitrile) that merged with the sample stream prior to entering the flow cell. All responses were recorded in at least triplicate.

2.2. Stopped-flow manifold

Experiments were performed with a flow manifold consisting of a programmable dual syringe pump (model sp201iw, WPI, Glen Waverly, Victoria, Australia) and a GloCel chemiluminescence detector (Global FIA, Fox Island, WA, USA). The detector incorporated a dual-inlet serpentine-channel reaction zone, which enabled the merging of solutions directly in front of the photomultiplier module (Electron Tubes model P30A-05) to capture the entire profile of chemiluminescence intensity over time. The 10 mL syringes were loaded with (i) aqueous 1×10^{-3} M $Ru(bipy)_3{}^{3+}$ reagent in 0.05 M sulfuric acid, and (ii) 1×10^{-5} M RDX in ethanol with 5% sulfuric acid. Precise volumes (120 μL) of the reagent and analyte solutions were dispensed (167 $\mu L\,s^{-1}$), propelling both solutions into the reaction channel, where the mixture was held for a set period of time. The output signal was recorded using an e-corder 410 data acquisition system (eDAQ, Denistone East, NSW, Australia).

2.3. Modelling chemiluminescence intensity versus time profiles

The experimental data were fitted to a model comprising the sum of two independent components, each based on the ‘double exponential’ description of chemiluminescence [36,37]. This involves two sequential, irreversible, pseudo-first-order reactions ($A \rightarrow B \rightarrow C$), where A, B and C represent pools of reactants, intermediates and products, respectively, and chemiluminescence intensity is proportional to pool B. The corresponding differential rate laws were numerically integrated using a first-order Euler method [38,39]. The parameters were varied using a simplex algorithm implemented in the Solver feature in Microsoft Excel, until the variability ($SS = \sum_{i=1}^{N} (Expt_i - Fit_i)^2$, where N is the number of data points) between the experimental and fitted data was minimized.

2.4. Reagents

All chemicals were of analytical grade unless otherwise stated. RDX was obtained from the Australian Federal Police (Grade A, Batch R617, 19-12-03). This was kept in deionised water and stored at approximately 4 °C. Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX), 2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane (CL-20), isopropyl nitrate (IPN) and pentaerythritol tetranitrate (PETN) (1 mM stock solutions in ethanol) were supplied by the Defence Science and Technology Organisation (Australia). Zinc (20-mesh, 99.8+%) and mercury chloride (99.5%) were obtained from Sigma–Aldrich (St Louis, MO, USA). Lead dioxide and ethanol (99.8%, w/w) were obtained from Ajax (Sydney, New South Wales, Australia). Sulfuric acid (98%, w/w) was obtained from Rhone-Poulenc (Victoria, Australia). Tris(2,2′-bipyridyl)ruthenium(II) chloride hexahydrate (≥98%) was obtained from Strem Chemicals (Newburyport, MA, USA). Acetonitrile (Isocratic, HPLC grade) was obtained from Scharlau Chemicals (Barcelona, Spain). Compounds used in the interference study (other than those listed above) were obtained from Sigma–Aldrich.

The tris(2,2′-bipyridyl)ruthenium(III) reagent was prepared by the addition of tris(2,2′-bipyridyl)ruthenium(II) chloride hexahydrate ($Ru(bipy)_3Cl_2 \cdot 6H_2O$; 7.49×10^{-2} g) to 0.05 M sulfuric acid (100 mL), followed by the addition of excess lead dioxide (~50 mg), with occasional swirling for 15 min. The flow injection analysis experiments were conducted within 45 min of preparing the reagent, which was passed through a 45 μm nylon filter (Tuffyn membrane; Pall, Cheltenham, Victoria, Australia) to remove excess oxidant shortly prior to use. Deionised water was obtained using a Continental Water Systems (RO 300, Melbourne, Victoria, Australia) complemented by a high purity reverse osmosis system with a Kinetico Mach Series pre-treatment system. Where specified, solutions were ultrasonicated using an Ultrasonic Cleaner, Type FX14P, 50 Hz (Unisonics, Sydney, Australia).

2.5. Preparation of zinc amalgam

Zinc (20-mesh; 1 g) was added to an aqueous solution of mercuric chloride (2%, w/v, 5 mL) [40,41]. This mixture was gently agitated with a glass rod until the solution was a murky grey (~10 min). The resultant solution was decanted before repeated washing with deionised water (4 × 5 mL) until clear. The zinc amalgam was stored under deionised water (at room temperature) until needed. Before use, the zinc amalgam was activated by decanting the water and washing with the required solvent (4 × 5 mL). It was then agitated until it appeared silver and lustrous.

Table 2
Chemiluminescence signal with 1 mM $Ru(bipy)_3^{3+}$ (aqueous solution with 0.05 M H_2SO_4), using flow injection analysis methodology to merge the reduced analyte (or 'blank' mixture) with the chemiluminescence reagent.

Reductant	Solvent	Signal (mV)	Blank (mV)	Signal-to-blank ratio
None	Ethanol	3.9	7.8	0.5
None	Ethanol (H_2SO_4)	6.6	3.1	2.1
Tin (II)	Ethanol	26,250	26,250	1
Titanium (III)	Ethanol	32.1	23.7	1.4
Devarda's alloy	Ethanol	10.7	5.5	1.9
Zn amalgam	Ethanol (H_2SO_4)	171	4.3	40

2.6. Preliminary procedures

In the case of the metal salts (tin(II) chloride, titanium(III) sulfate), the reductant was dissolved in ethanol or acetonitrile, added to the analyte solution (approximately 1 mM RDX in ethanol or acetonitrile) and allowed to react for up to 30 min. Alternatively, the zinc amalgam and Devarda's alloy were loaded into a column with glass frit and tap. The RDX solution was added into the column, allowed to stand for up to 30 min, and then sampled by opening the tap. Aliquots of the reaction mixtures or eluted solutions were combined with the chemiluminescence reagent using the flow-injection analysis system described above. 'Blank' samples were obtained by performing the same reduction step on the solvent (without RDX).

3. Results and discussion

3.1. Comparison of reducing agents

McHugh et al. [33] previously examined twelve reagents for the controlled reduction of RDX. Although the mechanisms of these reactions are yet to be elucidated, the identification of several intermediates and products by NMR analysis clearly showed that the reduction route was highly reagent dependent. Seeking derivatives suitable for the preparation of SERRS active species, McHugh et al. [33] identified three promising reactions: reduction by borohydride or palladium-catalysed hydrogenation to give hexamethylenetetramine, or reduction by sodium amalgam to give hydrazine. Reduction of RDX with zinc dust to generate nitrous acid [42] or ammonia and low molecular weight amines [43] (followed by Griess [42] or Berthelot [43] reactions) has been utilised for spectrophotometric determinations. For the proposed chemiluminescence detection, however, the reducing agent must: (i) generate at least one species from RDX that elicits intense chemiluminescence with $Ru(bipy)_3^{3+}$; (ii) react with the analyte at a rate that is suitable for screening purposes; and (iii) produce no light upon reaction with $Ru(bipy)_3^{3+}$ or be easily removed from the reaction mixture.

The chemiluminescence responses for RDX (approximately 1 mM in ethanol), untreated or treated with a reducing agent (tin(II) chloride, titanium(III) sulfate, Devarda's alloy and zinc amalgam) were examined (Table 2). Each of these reagents has previously been used for the reduction of nitro-compounds [40]. The analyte solution treated with tin(II) chloride produced an intense emission with $Ru(bipy)_3^{3+}$ (over three orders of magnitude greater than the untreated sample), but the response was almost exclusively derived from the reaction of $Ru(bipy)_3^{3+}$ with excess reductant. Although unfavourable for the detection of RDX, this finding was exploited for the first direct chemiluminescence detection of a metal ion with $Ru(bipy)_3^{3+}$, which has since been applied to the rapid determination of tin(II) in dental products [35]. RDX treated with titanium(III) sulfate produced a signal that was eight-fold greater than the untreated sample, but again a significant portion (~75%) of the emission was attributed to the excess reductant in the analyte solution.

Unlike the metal salts, the alloys did not remain in the sample solution when merged with the chemiluminescence reagent, and therefore only minor differences in the signals for the blank solution with and without the reduction step were observed. The RDX solutions treated with Devarda's alloy or the zinc amalgam produced greater signals than the untreated analyte. As the zinc amalgam provided the greatest increase (approximately 40-fold with respect to blank and 26 fold with respect to untreated analyte), it was selected for further investigation.

3.2. Reaction conditions and figures of merit

To examine the effect of reduction time on maximum chemiluminescence intensity (peak height), RDX (5×10^{-5} M) in 100 mL ethanol/H_2SO_4 (in a beaker) was treated with the activated zinc amalgam (prepared from 1 g of zinc). Samples were periodically taken (at 3 min intervals) by syringe through a 0.45 μm filter and immediately combined with the chemiluminescence reagent using flow injection analysis methodology. The intensities were found to increase as aliquots were taken over the first 25 min and then remain reasonably steady until 40 min (at approximately 10-fold that of the untreated RDX), before decreasing to values similar to the blank signal by 90 min. It should be noted, however, that the reaction of each aliquot (containing reduced RDX) with the chemiluminescence reagent was by comparison very fast—the maximum intensity was reached within 2 s under stopped-flow conditions. The greatest signals using flow injection analysis were therefore obtained using a short length of tubing (~1 cm) between the confluence point and the detection coil, and flow rates of 3 mL min^{-1} per line. Additional aliquots removed from the reducing mixture at various times and left overnight before combining with the chemiluminescence reagent did not elicit a significant response above the blank signal. Similar results were observed using acetonitrile rather than ethanol.

Not surprisingly, ultrasonication of the RDX reduction increased the rates of formation of species capable of eliciting emission upon reaction with $Ru(bipy)_3^{3+}$ (Fig. 2) [44]. The greatest chemiluminescence response was obtained when the sample was treated with the zinc amalgam and ultrasonicated for 12 min. A calibration prepared with nine RDX standard solutions between 1×10^{-8} M and 1×10^{-4} M showed an approximately linear relationship ($R^2 = 0.9833$) between the logarithms of intensity and concentration. The reproducibility of the reduction step was reasonable, with a relative standard deviation of 8.7% obtained for seven replicates of a 1×10^{-6} M RDX standard. Moreover, the relative standard deviation for replicate injections of each reduced RDX solution was routinely below 2%. The limit of detection (blank response + 3σ, accounting for the error associated with both the off-line reduction and flow-injection analysis steps) was 1×10^{-8} M.

3.3. Chemiluminescence profiles under stopped-flow conditions

Examination of the entire emission profile of the reaction of $Ru(bipy)_3^{3+}$ with reduced RDX revealed two distinct phases of the reaction: a sharp rise and fall in intensity over the first

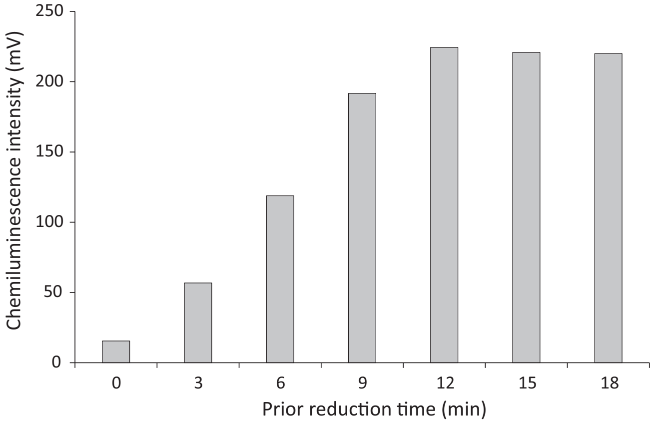

Fig. 2. Chemiluminescence intensity for the reaction of $Ru(bipy)_3{}^{3+}$ with 5×10^{-5} M RDX, after the analyte was reduced with zinc amalgam in a beaker with ultrasonication for various periods of time. The small 'blank' response was subtracted from each signal.

Table 3
Fitted parameters for the model of chemiluminescence intensity versus time profiles for the reaction of 1×10^{-5} M RDX with 1 mM $Ru(bipy)_3{}^{3+}$, under stopped-flow conditions, after the analyte was reduced with zinc amalgam for 5 min or 12 min, as depicted in Fig. 3.

Parameter	5 min	12 min
A_0	18.55	41.76
k^1	2.47	1.19
k^2	0.186	0.181
A'_0	11.7	36.00
$k^{1\prime}$	0.0352	0.0337
$k^{2\prime}$	0.0352	0.0337

10 s, followed by a plateau and slow decay to baseline signal (Fig. 3a). Similar chemiluminescence intensity–time profiles were reported by He et al. [45,46] when combining binary mixtures of analytes (such as oxalic and tartaric acid) with $Ru(bipy)_3{}^{2+}$ and cerium(IV). This suggests that there were at least two products of the RDX reduction capable of producing light with $Ru(bipy)_3{}^{3+}$. Moreover, a model comprising the sum of two independent components, each characterised by the classic 'double exponential' description of chemiluminescence reactions [36,37], provided an excellent fit of the experimental data (Fig. 3b and Table 3). The relatively long second phase of the light-producing reaction with reduced RDX was not observed in the blank signal, suggesting that greater signal-to-blank ratios could be obtained by increasing the distance between the confluence and detection points of the FIA manifold (to capture a later portion of the profile), albeit with a corresponding decrease in peak height and sample throughput.

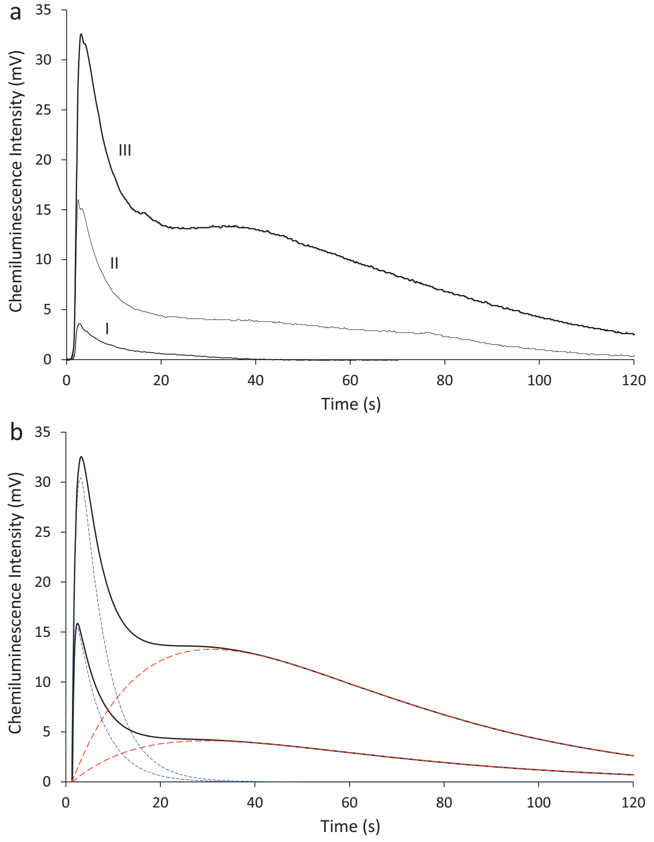

Fig. 3. (a) Chemiluminescence intensity versus time profiles obtained under stopped-flow conditions when the $Ru(bipy)_3{}^{3+}$ reagent was combined with (I) blank solution, (II) RDX after a 5 min reduction step, and (III) RDX after a 12 min reduction step. (b) Fitted models of profiles II and III, each comprising the sum of responses from two major RDX-reduction products capable of producing light upon reaction with $Ru(bipy)_3{}^{3+}$. The dotted lines in (b) represent the deconvoluted profiles for the contributing species. See Table 3 for the individual parameters.

3.4. Comparison with related compounds

To establish the essential structural requirements for the observed response from reduced RDX, we tested two closely related nitramine explosives (HMX and CL-20; Fig. 1) and 16 other compounds possessing NO_2 and/or NH_2 groups, including those shown in Fig. 4. Of these, only HMX and CL-20 gave significant responses (19% and 159% of that observed for RDX) when subjected to the same zinc amalgam reduction and FIA-chemiluminescence

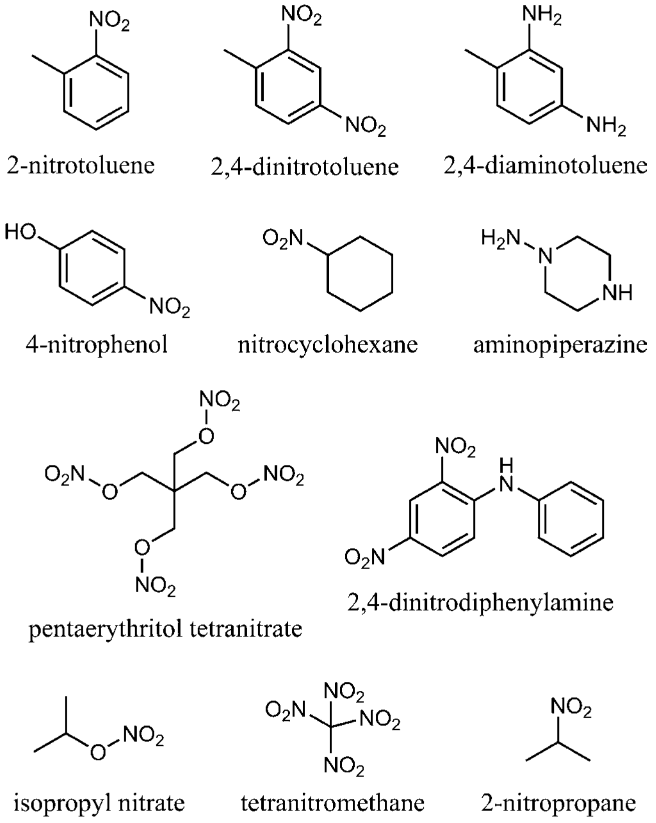

Fig. 4. Examples of compounds possessing NO_2 or NH_2 groups that were tested with the reduction–chemiluminescence detection procedure.

detection procedure (using an analyte concentration of 5×10^{-5} M). Examination of the light-producing reactions under stopped-flow conditions (Figure S1 in ESI) again revealed that multiple species capable of producing light with the $Ru(bipy)_3^{3+}$ reagent were generated in the initial reduction step. In the case of CL-20, the chemiluminescence–intensity time profiles appeared to be more representative of a single light-producing pathway, but we obtained a much better fit with a model incorporating two intermediates with distinct rates of reaction. In the case of HMX, more complex kinetics were observed, due to a greater contribution from species that react at slower rates with the chemiluminescence reagent. No significant signal above the blank was observed from any of the other compounds tested, with the exception of small responses from 1×10^{-3} M 2,4-dinitrotoluene and 2,4-diaminotoluene of 14 and 12 mV (after blank subtraction), which were lower than the signal obtained for 1×10^{-7} M RDX (17 mV).

4. Conclusions

A novel approach to detect RDX and related explosives utilising $Ru(bipy)_3^{3+}$ chemiluminescence has been established. The procedure exhibits considerable selectivity towards nitramine ($N\text{-}NO_2$) compounds, with very little or no response observed from a wide range of aromatic and aliphatic compounds possessing NH_2, NO_2, $O\text{-}NO_2$ and/or $N\text{-}NH_2$ groups. Furthermore, it was performed using simple, low-cost instrumentation suitable to be scaled-down for at-scene applications. Distinction from potential environmental interferences (such as aliphatic tertiary amines) that produce light with this reagent without the zinc amalgam reduction may necessitate some degree of physical separation, but might also be derived from the change in emission intensity before and after the reduction step. We anticipate further advances in this approach to be gained from the application of high-surface area microreactors to automate and accelerate the reduction step, and spectroscopic exploration of the key intermediates formed in the reduction process that are responsible for the subsequent intense emission of light with $Ru(bipy)_3^{3+}$.

Acknowledgements

The authors thank the Australian Federal Police for providing RDX samples. P.S.F. acknowledges ARC Future Fellowship funding. D.N.D. would like to thank Jessica Terry (Deakin University) for her assistance during the stopped-flow experiments.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.talanta.2011.11.051.

References

[1] M. Pumera, Electrophoresis 27 (2006) 244.
[2] M.S. Meaney, V.L. McGuffin, Anal. Bioanal. Chem. 391 (2008) 2557.
[3] M.E. Germain, M.J. Knapp, Chem. Soc. Rev. 38 (2009) 2543.
[4] J. Wang, Anal. Chim. Acta 507 (2004) 3.
[5] C. Sarazin, N. Delaunay, A. Varenne, C. Costanza, V. Eudes, P. Gareil, Sep. Purif. Rev. 39 (2010) 63.
[6] S. Götz, U. Karst, Anal. Bioanal. Chem. 387 (2007) 183.
[7] J. Yan, X. Yang, E. Wang, Anal. Bioanal. Chem. 381 (2005) 48.
[8] X.-B. Yin, S. Dong, E. Wang, Trends Anal. Chem. 23 (2004) 432.
[9] P.S. Francis, C.F. Hogan, in: I.D. McKelvie, S.D. Kolev (Eds.), Advances in Flow Injection Analysis and Related Techniques, Comprehensive Analytical Chemistry Series, vol. 54, Elsevier, Oxford, 2008, p. 343.
[10] M.M. Richter, Chem. Rev. 104 (2004) 3003.
[11] B.A. Gorman, P.S. Francis, N.W. Barnett, Analyst 131 (2006) 616.
[12] H. Wei, E. Wang, Trends Anal. Chem. 27 (2008) 447.
[13] W. Miao, Chem. Rev. 108 (2008) 2506.
[14] P.S. Francis, J.L. Adcock, J.W. Costin, S.D. Purcell, F.M. Pfeffer, N.W. Barnett, J. Pharm. Biomed. Anal. 48 (2008) 508.
[15] C.M. Hindson, G.R. Hanson, P.S. Francis, J.L. Adcock, N.W. Barnett, Chem. Eur. J. 17 (2011) 8018.
[16] I. Rubinstein, A.J. Bard, J. Am. Chem. Soc. 103 (1981) 512.
[17] J.D. Debad, E.N. Glezer, J. Wohlstadter, G.B. Sigal, J.K. Leland, in: A.J. Bard (Ed.), Electrogenerated Chemiluminescence, Marcel Dekker, New York, 2004, p. 359.
[18] N.D. Danielson, in: A.J. Bard (Ed.), Electrogenerated Chemiluminescence, Marcel Dekker, New York, 2004, p. 397.
[19] D.R. Skotty, W.-Y. Lee, T.A. Nieman, Anal. Chem. 68 (1996) 1530.
[20] K. Yokota, K. Saito, S. Yamazaki, A. Muromatsu, Anal. Lett. 35 (2002) 185.
[21] K. Uchikura, Chem. Pharm. Bull. 51 (2003) 1092.
[22] K. Uchikura, M. Kirisawa, A. Sugii, Anal. Sci. 9 (1993) 121.
[23] S. Yamazaki, K. Ban'i, T. Tanimura, J. High Resolut. Chromatogr. 22 (1999) 487.
[24] N. Niina, H. Kodamatani, K. Uozumi, Y. Kokufu, K. Saito, S. Yamazaki, Anal. Sci. 21 (2005) 497.
[25] M.E. Bolden, N.D. Danielson, J. Chromatogr., A 828 (1998) 421.
[26] K. Uchikura, Chem. Lett. 32 (2003) 98.
[27] F.E.O. Suliman, M.M. Al-Hinai, S.M.Z. Al-Kindy, S.B. Salama, Talanta 74 (2008) 1256.
[28] T. Pérez-Ruiz, C. Martínez Lozano, V. Tomás, J. Martín, J. Chromatogr., A 1077 (2005) 49.
[29] T. Pérez-Ruiz, C. Martínez-Lozano, M.D. García, J. Chromatogr., A 1164 (2007) 174.
[30] H. Morita, M. Konishi, Anal. Chem. 75 (2003) 940.
[31] K. Uchikura, Anal. Sci. 16 (2000) 453.
[32] H. Kodamatani, H. Shimizu, K. Saito, S. Yamazaki, Y. Tanaka, J. Chromatogr., A 1102 (2006) 200.
[33] C.J. McHugh, W.E. Smith, R. Lacey, D. Graham, Chem. Commun. (2002) 2514.
[34] S.J. Woltman, W.R. Even, E. Sahlin, S.G. Weber, Anal. Chem. 72 (2000) 4928.
[35] M.E. Gange, S.C. Parratt, P. Jones, P.S. Francis, N.W. Barnett, Analyst 134 (2009) 2397.
[36] M. Orlovic, R.L. Schowen, R.S. Givens, F. Alvarez, B. Matuszewski, N. Parekh, J. Org. Chem. 54 (1989) 3606.
[37] R.E. Milofsky, J.W. Birks, J. Am. Chem. Soc. 113 (1991) 9715.
[38] J. Stewart, Calculus, 4th ed., Brooks/Cole, Pacific Grove, CA, 1999.
[39] M.C.R. Cockett, G. Doggett, Maths for Chemists, vol. 1, Royal Society of Chemistry, Cambridge, UK, 2003.
[40] M. Hudlický, Reductions in Organic Chemistry, American Chemical Society, Washington, DC, 1996.
[41] A.I. Vogel, Vogel's Textbook of Quantitative Inorganic Analysis: Including Elementary Instrumental Analysis, Longman Scientific & Technical, London, 1978.
[42] T.F. Jenkins, M.E. Walsh, Talanta 39 (1992) 419.
[43] A. Uzer, E. Ercag, R. Apak, Anal. Chim. Acta 612 (2008) 53.
[44] J.L. Luche, C. Bianchi, Synthetic Organic Sonochemistry, Plenum, New York, 1998.
[45] Z. He, H. Gao, L. Yuan, Q. Luo, Y. Zeng, Analyst 122 (1997) 1343.
[46] Z. He, X. Li, H. Meng, S. Lu, G. Song, L. Yuan, Y.E. Zeng, Anal. Lett. 31 (1998) 1553.