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The first controlled reduction of the high explosive RDX†

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The first reduction chemistry of the high explosive RDX that allows subsequent functionalization into a SERRS active species.

In the modern fight against terrorism, the detection of hidden high explosives by determining the presence of their vapour in the atmosphere is an important tool.[1–5] However, many of the most widely used explosives have very low vapor pressures and concealment of the explosive in suitable wrapping further reduces the effective concentration in the atmosphere.[3] Current methods of detection use a vapor collection system to sample air space, followed by detection using methods such as ion mobility spectrometry,[3,6,7] mass spectrometry,[8] trained dogs,[1,9] gas chromatography with thermal energy analysis or electron capture detection, [1,10,11] biosensors[12–15] and chemosensors.[16] Although these techniques are very sensitive, there is still a need for improvements in sensitivity, simplicity and speed. SERRS is one of the few techniques not currently used, which has the potential to deliver the improvements required. This is indicated by recent reports that demonstrate that SERRS can be used in a sensitive and quantitative manner for other analytes.[17–19]

One of the key high explosives for which a good analytical method is required is 1,3,5-trinitro-1,3,5-triazacylcohexane (RDX), which is a major constituent of the plastic explosive Semtex. In this study, we report the first controlled reduction of RDX in an attempt to devise a method of detection similar to that previously adopted for TNT.[20] The method adopted for TNT selectively reduced one nitro group which was then used to form an azo dye to produce a species that gave excellent surface enhanced resonance Raman scattering, SERRS, at trace levels. TNT is a widely studied molecule and there was a substantial amount of prior research to guide us in the chemistry. However, the chemistry of RDX has received very little study and as such all of the chemistry reported herein is novel.

RDX does not produce good SERRS and requires chemical manipulation to provide signals at levels approaching those of interest for sensitive detection. The RDX molecule has three secondary nitramine functions, which were targeted as points for functionalization. RDX is a highly stable molecule under a wide variety of chemical conditions but it rapidly decomposes under others. Thus, reaction of the acidic methylene protons with base tends to afford only ubiquitous products such as formaldehyde, ammonia, nitrite and other inorganics.[21] Due to the lack of available literature for the chemical reduction of secondary nitramines a range of reducing agents were investigated for the selective reduction of RDX. (Table 1.)

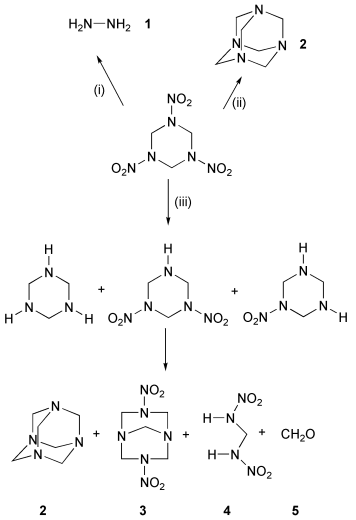
The methods examined revealed that the chemical reduction of RDX was a complex process although selective control over the products could be achieved through choice of the reducing agent. Of the twelve reduction methods employed, seven gave successful and unprecedented reductions of RDX. Three of the reduction routes gave derivatives that could easily be used to prepare SERRS active species. These were reduction by sodium amalgam to give hydrazine, palladium catalyzed hydrogenation to give unstable intermediates that rearranged to hexamethylenetetramine, and reduction by borohydrides that also gave hexamethylenetetramine. (Scheme 1)

Hexamethylenetetramine is known to react with diazonium salts to form a diazononane derivative.[22–24] Use of diazotised groups commonly used for surface adsorption such as benzotriazole[25] and hydroxyquinoline[20] appeared to give small amounts of the desired product but were difficult to isolate and

Table 1 Reducing agents attempted with RDX

Reducing agent	Identified products[a]
Na(Hg)/THF/H_2O	Hydrazine (**1**) 1,3-Dinitro-5-hydro-1,3,5-triazine[b] 1-Nitro-3,5-dihydro-1,3,5-triazine[b] 1,3,5-Hexahydrotriazine[b] 3,7-Dinitro-1,3,5,7-tetraazabicyclononane[bc] (**3**) Methylenedinitramine[c] (**4**) Formaldehyde[c] (**5**)
H_2/Pd(C)	Hexamethylenetetramine[c] (**2**)
Borohydride exchange resin/ $Ni(OAc)_2$/MeOH	Hexamethylenetetramine (**2**)
$NaBH_4$/Pd(C)	Hexamethylenetetramine (**2**)
Zn/AcOH/$NO_2C_6H_4CHO$	*N*,*N*′,*N*″-Tris(2-nitrobenzylidene)-{1,3,5}triazinane-1,3,5-triamine
$CrCl_2$/DMF	Reaction observed, products not identified
Fe/AcOH	Reaction observed, products not identified
$NH_2NH_2.H_2O$/C	No reaction
$BF_3{\cdot}OEt_2$	No reaction
$NaBH_4$/AcOH	No reaction
MeOH/Pd(C)	No reaction

[a] Identification based on ^{1}H NMR analysis. [b] Initial unstable reduction products. [c] Decomposition products of initial unstable reduction products.



Scheme 1 *Reagents and conditions*: (i) Na(Hg)/THF/H_2O, 60 min; (ii) borohydride exchange resin/$Ni(OAc)_2$/MeOH, 180 min, 100%; (iii) H_2/Pd(C), 120 min.

† Electronic supplementary information (ESI) available: full experimental details on the synthesis and analysis of the reported compounds. See http://www.rsc.org/suppdata/cc/b2/b207885f/

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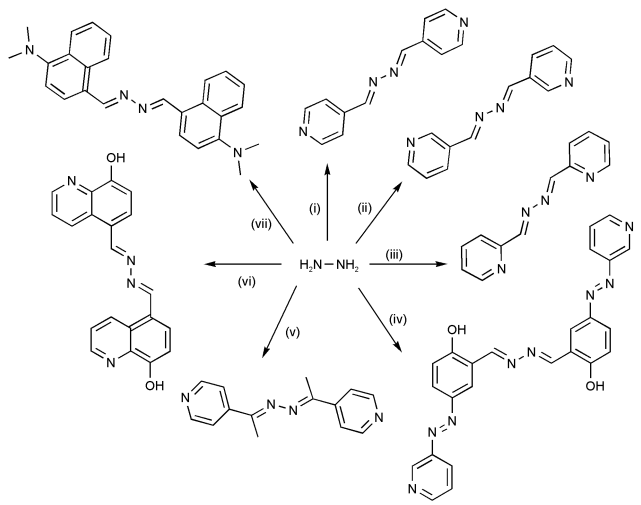
characterize. Due to the complexity of the reduction to produce the hexamethylenetetramine and the low yield of the subsequent derivatization, reduction by sodium amalgam to give hydrazine was favored. The reduction of RDX by sodium amalgam to give hydrazine is the first reported chemical transformation of this molecule that does not result in the cleavage of the N–N bond. It should be noted that a small amount of THF as a co-solvent to aid solubility of the RDX is necessary as without THF no reduction is observed.

The mechanism for the reduction of RDX by the sodium amalgam is unclear but based on our observations and those of others we propose the following. Initially the reduction of a nitro group to the amine occurs followed by base promoted collapse of the ring system to give hydrazine. A report by Duden and Scharff[26] indicated that 1,3,5-trinitroso-1,3,5-triazacyclohexane could be reduced to 1,3,5-triamino-2,4,6-hexahydro-*s*-triazine under similar conditions, however, this compound could only be isolated as the Schiff base derivative. Subsequent reports by Stolle,[27] Lamberton,[28] Bonner *et al.*[29] and Neilsen *et al.*[30] showed that these types of *s*-triazines were highly unstable hence supporting our proposed mechanism to give hydrazine. Additionally, electrochemical reductions of secondary nitramines give hydrazines via the N-nitroso derivatives supporting our proposed mechanism.[31] Further to this our experimental evidence from the reduction of RDX by hydrogenation indicated the presence of RDX minus one nitro group, which then rearranged to hexamine as the stable product. In the reduction by the sodium amalgam we could not detect any hexamine formation indicating that the mechanism was clearly different to that of the other reducing agents.

The trapping of the hydrazine with a number of different carbonyl functionalities was investigated. For the species to be useful for subsequent detection by SERRS it was desirable to incorporate a color into the final product. This was achieved through reaction of 2 mol of an aldehyde or ketone with 1 mol of hydrazine. If only 1 mol of the carbonyl reacts then a hydrazone was formed which was less favourable for SERRS. In total 16 aldehydes and ketones were used to trap the hydrazine and give coloured azines. The aldehydes and ketones were chosen on the basis of previous knowledge for the design of effective SERRS species and included surface complexing molecules such as pyridine and 8-hydroxyquinoline. Nine of the azines produced were discounted almost immediately due to the relatively low SERRS obtained. The remaining seven were examined in more detail (Scheme 2). All of the azines shown in Scheme 2 gave effective SERRS, however, the best signals were obtained from a specifically designed pyridine azo dye synthesized by azo coupling of diazotised *m*-aminopyridine with salicylaldehyde. Work into the ultra-sensitive detection of the hydrazine produced by controlled reduction of RDX will be reported soon as initial experiments indicate that detection of the azine by SERRS can be achieved at 10 femtomoles.



Scheme 2 *Reagents and conditions*: (i) *p*-C_5H_4NCHO, EtOH, 20 min, 75% (ii) *m*-C_5H_4NCHO, EtOH, 20 min, 64% (iii) *o*-C_5H_4NCHO, EtOH, 20 min, 93% (iv) *p*-$C_5H_4N(N_2)C_6H_3(OH)CHO$, EtOH, 20 min, 75% (v) *p*-$C_5H_4NCOCH_3$, EtOH, AcOH, Δ, 20 min, 50% (vi) 8-$HOC_{10}H_5NCHO$, EtOH, 20 min, 84% (vii) $(CH_3)_2NC_{10}H_6CHO$, EtOH, AcOH, Δ, 12 h, 47%.

In conclusion, the reduction of RDX has been examined in detail and a new route that maintains the N–N bond discovered. This allowed the formation of hydrazine from RDX as opposed to other compounds that are harder to derivatize for subsequent sensitive detection. Initial detection of the trapped products indicated that ultra-sensitive detection by SERRS was possible and shows considerable promise. It should be noted that the new chemistry described here would work with other techniques.

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