

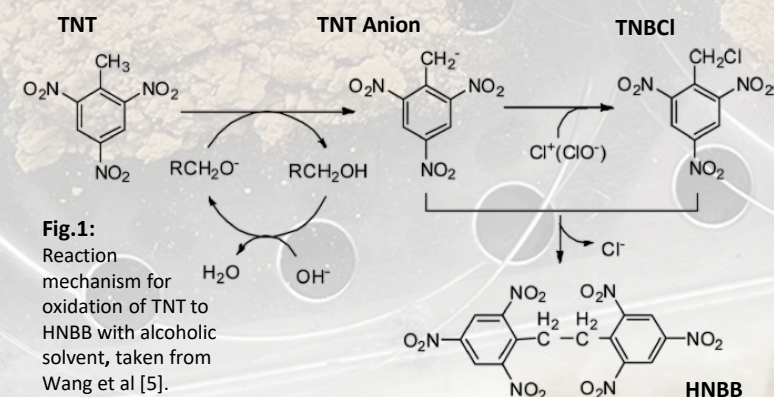
Improving Methods And Knowledge On The Synthesis Of Hexanitrobibenzyl For Hexanitrostilbene Production

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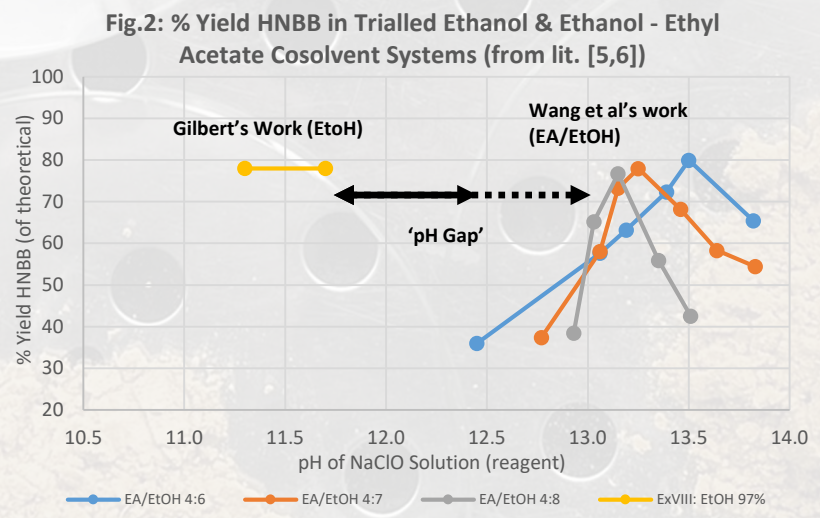
1. INTRODUCTION

Hexanitrostilbene (HNS) is a highly stable, heat and pressure resistant explosive molecule with specialist applications in the energetics sector [1,2,3]. Modern literature on its synthesis strongly suggests the 2-step synthesis route from trinitrotoluene (TNT) via the intermediary hexanitrobibenzyl (HNBB) is the most applicable pathway for manufacture [4,5,6,7], given its simplicity, the availability of TNT (trinitrotoluene), and the ability to utilise greener and less hazardous chemistries whilst maintain high yield and product purity [6]. This study investigated HNBB yield across varying reaction conditions for the first synthesis step, whereby TNT dissolved in alcoholic solvent is deprotonated and oxidised to HNBB upon addition of 5% sodium hypochlorite (NaClO) solution (see Fig.1).



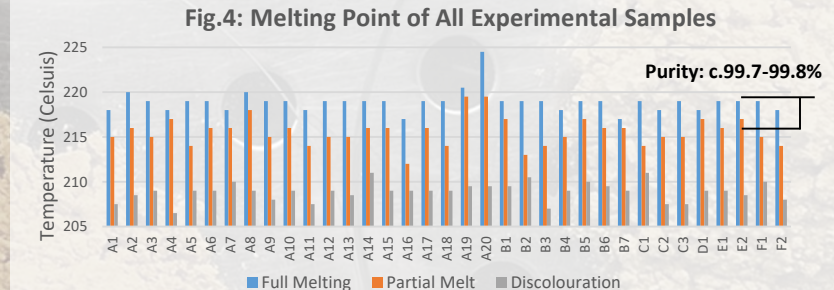
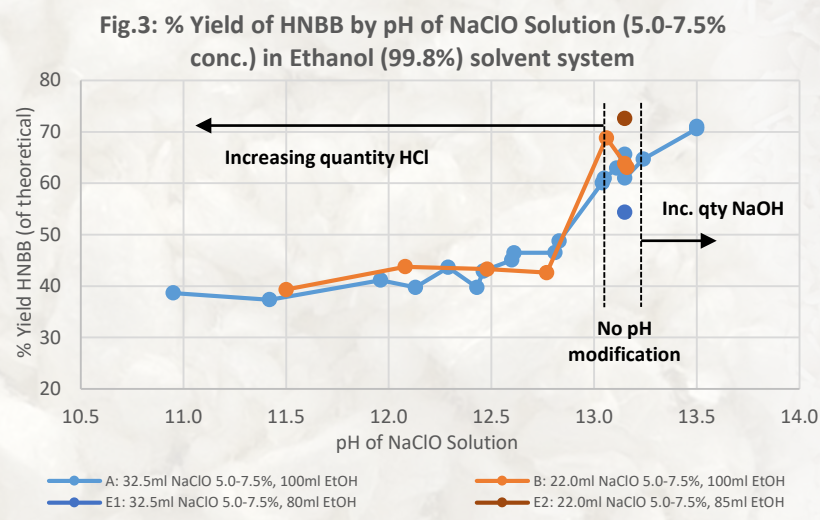
2. THE 'pH GAP'

Previous studies have determined pH of the NaClO solution to be a critical in determining HNBB yield, alongside choice of solvent system applied [5,6]. Further co-dependent variables such as reaction temperature and minimisation of solvent volume have also been proven to have significant effect [5]. Extensive work conducted by Wang et al has demonstrated the effect of NaClO solution pH on HNBB yield with ethanol – ethyl acetate cosolvent (EA/EtOH), finding an optimum in the pH 13.0-13.5 range [6]. However, Gilbert's work, where ethanol (EtOH) solvent was trialled provides only one example of reaction conditions suggesting an optimal NaClO solution pH of 11.3-11.7 [5]. This contrasts with the finding that stronger alkaline conditions are essential in allowing deprotonation of TNT to its anion [6], leaves a 'pH gap' in the literature from pH 11.7-12.7 where no yields have been reported with any solvent, and leaves the trend for HNBB yield by pH with the ethanol solvent system inadequately investigated (see Fig.2).



3. EXPERIMENTAL WORK & RESULTS

This study utilised pure EtOH (99.8%) solvent with 5g batches of TNT flake and modified pH of the NaClO solution in order to identify the trend of HNBB yield across the wider pH range 10.95-13.50. pH was modified by addition of dilute HCl (to reduce pH) and dilute NaOH (to increase pH). Varying quantities of NaClO solution (22.0ml & 32.5ml) at two concentrations (5.0-7.5% and 5.0-5.5%) were utilised to try and isolate effect of the pH variable from others (see Fig.3). Experimental runs were also conducted to identify optimised solvent volume and reaction temperature, and to emulate the conditions investigated by Wang et al for comparability. pH and ORP of the NaClO solution was measured to 0.01 units using a DTK PH-230SD logger with DTK 2017 Double Junction pH/Reference Electrode and ATC probe & DTK 2017-SD ORP probe. Melting point of solid products recovered from the reaction through vacuum filtration was analysed using a Stuart MP3 to determine identity as HNBB and assess purity.



4. KEY FINDINGS & CONCLUSIONS

HNBB yield by NaClO solution pH has been reported across the wider pH scale (10.95-13.5) for the first time with ethanol solvent (see Fig.3) ORP of NaClO solution was found to have a slight negative correlation with HNBB yield (and pH) suggesting that pH is the more critical factor for yield. Optimal NaClO solution pH with ethanol solvent has been identified as 13.1-13.5 (with yields of 61-72%), very likely disproving Gilbert's previously reported optimum yield (79%) at pH 11.3-11.7 [5]. This is concomitant with Wang et al's finding that higher pH increases yield through promoting deprotonation of TNT [6]. Optimal yields achieved with ethanol were slightly lower than those reported with use of ethyl acetate cosolvent (see Figs.2 & 3), supporting the theory that improved TNT solubility in the cosolvent system allows significant yield improvement through use of lower total solvent quantity [6]. However, results from this study suggest yield obtained with ethanol solvent is slightly less sensitive to pH than with ethyl acetate cosolvent. Furthermore, optimal pH roughly matched the unmodified pH of the NaClO solution. This therefore suggests ethanol solvent provides a potential advantage in production setups where precision pH modification/measurement would increase costs.

Further optimisation of HNBB yield with the ethanol solvent system was identified. Yield was 76% when using 85ml 99.8% ethanol and 22.0ml NaClO solution with 5g TNT - up from 65% when using 100ml ethanol (see Fig.3). This was despite the requirement for a higher temperature in order to ensure TNT dissolution, demonstrating that volume efficiency has greater effect on yield than temperature at commencing of the reaction [5]. Consistently high and narrow melting ranges (c.216-220°C, see Fig.4) of the HNBB products produced demonstrated high purity of c.99.7-99.8% [6]. For further volume efficiency, trialling of the reaction mechanism using newly-available sodium hypochlorite pentahydrate (NaClO.5H2O) as a replacement for NaClO solution is suggested [8]. Optimisation of reaction conditions with this oxidiser could lead to improved yields when using ethanol solvent since it has a lower pH than NaClO and the reaction mechanism appears to favour slightly lower pH with this solvent [6]. This would also provide the additional benefit of replacing NaClO solution with a less hazardous, less rapidly degrading and environmentally benign oxidiser [8].

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