Journal of Labelled Compounds and Radiopharmaceuticals
J. Labelled Cpd. Radiopharm. **42**, 1251-1264 (1999)

SYNTHESIS OF ^{14}C-LABELLED OCTAHYDRO-1,3,5,7-TETRANITRO-1,3,5,7-TETRAZOCINE (HMX) FOR USE IN MICROCOSM EXPERIMENTS

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KEYWORDS: ^{14}C-octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine; ^{14}C-HMX; ^{14}C-HMTA; ^{14}C-DAPT; ^{14}C-DADN; TAT;

SUMMARY

To monitor the biodegradation of explosives in microcosm experiments, carbon-14 labelled substrates such as ^{14}C-HMX were needed. Many synthetic routes were evaluated to identify the best synthesis of ^{14}C-HMX with high yield and minimal radioactive waste. To synthesize ^{14}C-HMX, acetylation of labelled hexamethylenetetramine (^{14}C-HMTA) was done yielding 3,7-diacetyl-1,3,5,7-tetraazabicyclo-[3.3.1]-nonane (^{14}C-DAPT) which was nitrated to obtain 1,5-diacetyloctahydro-3,7-dinitro-1,3,5,7-tetrazocine (^{14}C-DADN)

CCC 0362–4803/99/131251–14$17.50

Received 1 February 1999
Revised 25 March 1999
Accepted 1 June 1999

in one step. Nitrolysis of ^{14}C-DADN was achieved using a mixture of 100% nitric acid and phosphorus pentoxide to yield ^{14}C-HMX. The synthesis of this carbon-14 labelled HMX was optimized first using cold starting materials and then conducted with labelled compounds. This synthesis represents the best way of preparing high purity ^{14}C-HMX with a high yield.

INTRODUCTION

During this decade, many needs have already emerged related to identification, quantification, delimitation and elimination of energetic contaminants dispersed by munitions or, present in explosives dumps, trials or destruction fields, firing areas and production sites (1-2). Possible solutions for site decontamination include recycling, chemical treatment, incineration, or stabilization/encapsulation. Biotechnologies are presently being considered as viable treatment options for bioremediation of sites contaminated by explosives. These technologies utilize microorganisms to mineralize or to biodegrade organic contaminants into less hazardous compounds (3-4). Bioremediation has the advantage of being less expensive than incineration and is acceptable to the public. Within this context, a feasibility study was initiated on the biodegradation of selected energetic materials by microorganisms enriched from contaminated soils and a bioremediation biopile process was set up to mineralize RDX and HMX in contaminated soils (5-12). Before achieving bioremediation, the characterization of the contaminated sites was studied and appropriate sampling procedures were developed. (13-15).

To identify microorganisms capable of biodegrading or mineralizing explosives, laboratory-scale microcosm studies can be performed with ^{14}C-labelled explosives which represent the key products that allow the mineralization process to be monitored by the evolution of ^{14}C-carbon dioxide. Since radioactive explosives are not generally available

commercially, it was necessary to synthesize ^{14}C-labelled-RDX, TNT, NC, GAP (16) and ^{14}C-HMX for such a study. Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX, for High Melting Explosive) also called, octogen, homocyclonite and cyclotetramethylenetetramine, is the most powerful non-atomic explosive in military use and is much more expensive than RDX (17). It is used as a high explosive in octol mixtures which are comprised of 70% HMX and 30% TNT. When malfunction occurs with ammunition containing octol, the casing containing the shaped charge breaks into pieces upon impact with the target and spreads the octol mixture on the ground leading to contamination by HMX and TNT. This situation was frequently encountered on anti-tank ranges and is described in the literature (13-14). One should keep in mind that when synthesizing radioactive explosives, safety is of great concern to avoid personnel injury and radioactive contamination problems. Moreover, high yield routes must be used to avoid the disposal of radioactive explosive wastes and to optimize the use of expensive carbon-14 labelled starting materials. In order to achieve this, a safe and high yield synthetic route to ^{14}C-HMX was required.

To synthesize ^{14}C-HMX, all the available syntheses were examined and some of them were tried with cold materials to determine the best way to obtain HMX in high yield and purity. The synthetic route for the production of HMX is the process developed by Bachmann and Sheehan which was modified by Castorina *et al.* (18-20). This process leads to a mixture of HMX/RDX 73:27, (82% yield) that could be separated (17,21). Bulusu *et al.* used the Bachmann process to prepare RDX and HMX labelled with isotopes such as: ^{2}H, ^{15}N, ^{13}C and ^{18}O (22-24). Since they were interested in obtaining isotopic RDX and HMX, this process was suitable for their needs. In this study, our goal was to synthesize ^{14}C-HMX with a high yield avoiding purification procedures or

separation to minimize possible contamination and the generation of radioactive wastes.

The three synthetic routes developed by Gilbert *et al.* seemed more attractive to us since they claimed high yields for the steps involved in HMX synthesis (25,26). These three routes were described as the TAT, the DADN and the DANNO procedures. Lukasavage *et al.* also used tetraacetyl-1,3,5,7-tetrazocine (TAT) as a precursor for the HMX synthesis (27). TAT syntheses were described in the literature (28-29).

The route chosen to synthesize ^{14}C-HMX was the DADN procedure. This route involves the synthesis of DAPT. This step is exothermic and could be suppressed by the use of urea and, a recent study has proposed several alternatives to the use of urea as an exotherm suppressant (30,31). Since Shackelford *et al.* stated that a lot of precautions were required when using the nitric acid/polyphosphoric acid system to nitrolyse DADN, the 100% nitric acid/ phosphorus pentoxide system was chosen for our nitrolysis (32).

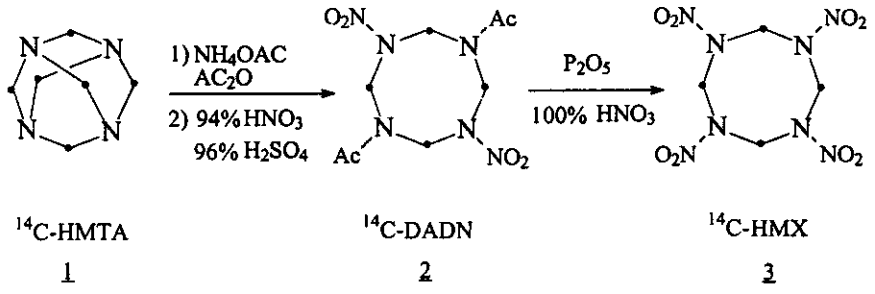
RESULTS AND DISCUSSION

Macro amounts of ^{14}C-HMX were prepared by mixing the available labelled starting material (^{14}C-formaldehyde) with its unlabelled homologue in sufficient quantity to obtain 2 g of ^{14}C-HMX at the end of this three-step synthesis.

Synthesis of ^{14}C-HMX

As mentioned, the DADN route was chosen for ^{14}C-HMX synthesis. Since this route consists of first acetylating and nitrolysing HMTA, it was necessary to synthesize ^{14}C-HMTA. The synthesis of ^{14}C-HMTA was performed using commercially available ^{14}C-formaldehyde (2 x 1mCi) mixed with unlabelled aqueous formaldehyde (37%) and reacted with concentrated ammonium hydroxide to yield ^{14}C-HMTA quantitatively (>99%) as reported in our earlier synthesis (16). Since ^{14}C-formaldehyde was mixed with unlabelled formaldehyde, the labelled carbons could be found statistically in HMTA rings,

where their possible locations are indicated by dots in figure 1. During the acetylation and nitration of HMTA to yield DADN, two methylenes were cleaved. This loss of carbons decreased the total radioactivity of the HMX end-product.



^{14}C-HMTA 1 ^{14}C-DADN 2 ^{14}C-HMX 3

Figure 1: Synthesis of ^{14}C-HMX

Acetylation and nitrolysis of this ^{14}C-HMTA yielded ^{14}C-DADN (88%). Infrared and NMR spectroscopy of the product were identical to the one of a known sample.(24). Nitrolysis of ^{14}C-DADN was performed using freshly distilled 100% nitric acid / phosphorus pentoxide at 50°C for 60 minutes followed by stirring at 28°C for 20 hours resulting in the production of pure ^{14}C-HMX (91%). It was observed that the strength of nitric acid had a direct impact on the yield of the reaction and that a small decrease in the strength had a great effect on the reaction. The phosphorus pentoxide concentration and the temperature were also very important parameters of the nitrolysis reaction. Infrared and NMR spectroscopy of the ^{14}C-HMX product demonstrated that it was identical to that of a commercial sample (17,32). No signals corresponding to DADN, at 5.5 and 2.3 ppm, were observed.

To identify the best route for the ^{14}C-HMX, all the available routes were tried with cold materials. From formaldehyde to HMX, the Bachmann process gives a mixture of

HMX/RDX with an overall yield of 85% yield while, in our hands, the DADN procedure and the TAT procedure gave respectively an overall yield of 89 and 80%. Using the radioactive materials, we were not able to reproduce the yields obtained with cold materials. The overall yield for our ^{14}C-HMX synthesis was 79%, which is lower than the Bachmann process but still this route represents the best choice since it yielded a pure product which did not have to be separated from a mixture.

Considering that a third of the labelled carbons are lost during the transformation of HMTA rings to DADN and that the overall yield for our ^{14}C-HMX is 79%, a theoretical amount of 1.05 mCi of activity should be obtained for the ^{14}C HMX sample assuming a radiochemical yield of 100%. Liquid scintillation counting revealed a total activity of 675μCi for our ^{14}C-HMX sample. Nevertheless, the ^{14}C-HMX, even with a total activity of 675 μCi, had a level of radioactivity high enough to be used in the biodegradation study.

EXPERIMENTAL

All solvents were purchased from Fisher Scientific Co. except anhydrous ethanol, which was obtained from "Les alcools de commerce limitée". Chemicals and starting materials such as aqueous formaldehyde and phosphorus pentoxide were purchased from Aldrich Chemical Co. The acids and bases were purchased from Baker except fuming nitric acid and red fuming nitric acid which were purchased from Aldrich Chem. Co. Fuming sulfuric acid (20% oleum) was purchased from ACP Chem. Co. Finally, ^{14}C-formaldehyde (58 mCi/mmol, 1mCi/mL) was obtained from Sigma Chemical. Co.

Infrared absorption spectra were registered with a Perkin-Elmer IR spectrophotometer (model 580) or with a Digilab FTS-40 spectrophotometer combined

with a DTGS detector. The infrared spectra for the solids were recorded using solid suspensions in KBr. ^{1}H and ^{13}C Nuclear magnetic resonance spectra were obtained from a Varian Gemini spectrometer (200 MHz). Spectra were recorded using deuterated chloroform or deuterated dimethyl sulfoxide as the solvent and tetramethylsilane as the internal reference at 0.0 ppm on the δ scale.

To identify the best route for the synthesis of ^{14}C-HMX, preparations of HMTA, DAPT, DADN, TAT and HMX were performed using cold starting materials according to known procedures and the yields were in agreement with the ones reported in the literature (24-28, 32). In all instances, chemical purity was assessed using IR and NMR spectroscopy compared to the literature (24-28, 32). HMTA was obtained with yield >99% as reported earlier (16), DAPT was obtained from HMTA with a yield of 92% (m.p.: 190-192°C, lit m.p.:192°C, 193-195°C, (25, 33). The spectroscopic analysis for this product is as follows: (IR: γ_{max} (KBr) cm^{-1}: 3420, 3000, 2920, 2880, 1625, 1480, 1460, 1430, 1385, 1380, 1350, 1320, 1310, 1210, 1190, 1080, 1020, 990, 970, 950, 940, 830, 810, 780, 680, 640, 600, 590, 580, 510, 480, 390. ^{1}H NMR: δ ($CDCl_3$) ppm : 5.64 (d, 2H, J=15 Hz, $NC\underline{H}_AH_BNAc$), 4.76 (system AB, 4H, j=15Hz, $NCH_A\underline{H}_BNAc$), 4.14 (s, 2H, NCH_2N), 4.13 (d, 2H, j=15 Hz, the other two $NC\underline{H}_AH_BNAc$), 1.98 (s, 6H, CH_3). ^{13}C NMR: δ ($CDCl_3$) ppm : 169.9 (CO, acetyl), 71.1 (NCH_2N), 67.5 (two NCH_2NAc) 62.9 (the two other NCH_2NAc), 21.9 (CH_3).

DADN was synthesized directly from HMTA (95% yield) while TAT was prepared from DAPT at a 92% yield. The melting point of TAT was 157-158°C (lit m.p.: 153-158°C, (24) and the spectroscopic analysis was as follows: IR: γ_{max} (KBr) cm^{-1}: 3420, 3020, 2995, 2940, 1650, 1490, 1420, 1380, 1340, 1300, 1260, 1230, 1210, 1180, 1110,

1060, 1040, 980, 940, 920, 820, 780, 620, 580, 540, 490. ^{1}H NMR: δ ($CDCl_3$) ppm : 5.08 (s, 8H, CH_2), 2.32 (s, 12H, CH_3). ^{13}C NMR: δ ($CDCl_3$) ppm : 172.2 (CO, acetyl), 59.5 (CH_2), 22.9 (CH_3).

HMX was synthesized from TAT and from DADN using either nitric acid/polyphosphoric acids or nitric acid/phosphorus pentoxide system for the nitrolysis with HMX yields varying from 67 to 94%. The parameters for the nitrolysis were in accordance with the Lukasavage process or the Gilbert procedure (24, 26). The best results obtained with the nitric acid/phosphorus pentoxide conditions were used for ^{14}C-HMX synthesis and are described. Nitric acid 100% was obtained by distilling concentrated nitric acid in the presence of concentrated sulfuric acid.

^{14}C-Hexamethylenetetramine (^{14}C-HMTA)

^{14}C-Formaldehyde (2 mCi, 58 mCi/mmole, 2 x 1mCi/mL) was quantitatively transferred into a three-neck flask (25 mL) containing unlabelled aqueous formaldehyde (37%) (5.92g, 0.0729 mole) and the flask was immersed in a water bath at 18°C. Concentrated ammonium hydroxide (3.8mL) was added dropwise for 30 minutes in order to maintain a temperature between 28 and 35°C. This solution was heated at 33-35°C for 24 hours and then transferred to a flask (250 mL) into which water was added to precipitate the product. The glassware was thoroughly washed to avoid contamination and the rinse water was added to the flask. Water was evaporated to yield ^{14}C-HMTA (1.70 g, >99%, mp: 268-272°C, decomposes). IR: γ_{max} (KBr) cm^{-1}: 2960, 2940, 2880, 1460, 1440, 1370, 1240, 1000, 810, 670. ^{1}H NMR: δ ($CDCl_3$) ppm: 4.73 (all protons,s). ^{13}C NMR: δ ($CDCl_3$) ppm : 74.8 (all carbons).

^{14}C-1,5-Diacetyloctahydro-3,7-Dinitro-1,3,5,7-Tetrazocine (^{14}C-DADN)

In a three-neck flask (25 mL) equipped with a reflux condenser and a magnetic stirrer, ^{14}C-HMTA (1.5936 g , 0.0113 mole) and ammonium acetate (0.7044 g, 0.0091 mole) were added to water (0.7968 g) at 5-10°C. To this stirred solution acetic anhydride (3.48 g, 0.0340 mole) was added dropwise over 60 minutes at 5-10°C. This DAPT solution was stirred at 5-10°C for an additional 30 minutes and transferred to an addition funnel. This solution was added dropwise over 80 minutes to a vigorously mechanically stirred mixture of 94% fuming nitric acid (7.17 g, 0.1052 mole) and 96% fuming sulfuric acid 20% oleum, (25.15 g, 0.2412 mole) at 18-20°C. After stirring for 20 minutes at 20°C, the solution was mixed with ice (230 g). The product precipitated with dilution with another 250 mL water. The product was filtered, washed and dried to yield ^{14}C-DADN (2.889 g, 0.0099 mole, 88% yield, m.p: 265°C, lit. 265°C, (23). IR: γ_{max} (KBr) cm^{-1}: 3400, 3020, 2940, 1675, 1520,1470, 1440, 1420, 1400, 1370, 1340, 1270, 1180, 1120, 1080, 1020, 990, 970, 940, 860, 810, 790, 760, 730, 620, 585, 510, 400, 390. ^{1}H NMR: δ (DMSO-$_{D6}$) ppm: 5.54 (m, 8H, methylene), 2.27 (S, 6H, CH_3). ^{13}C NMR: δ (DMSO-$_{D6}$) ppm: 165.0 (CO, acetyl), 61.9, 59.8 (CH_2), 21.6 (CH_3).

^{14}C-Octahydro-1,3,5,7-Tetranitro-1,3,5,7-Tetrazocine (^{14}C-HMX)

In a three-neck flask (250 mL) equipped with a mechanical stirrer and containing a mixture of 100% nitric acid (72.25 g, 1.15 mole) and phosphorus pentoxide (24.3 g, 0.0855 mole) was added ^{14}C-DADN (2.89 g, 0.0099 mole). This solution was stirred at 50°C for one hour then at room temperature for 20 hours. The solution was poured onto crushed ice (200 g) and the product was precipitated by adding water (800 mL). The suspension was kept at -4°C overnight and then the product was filtered, washed and air

dried to yield pure ^{14}C-HMX (2.68 g, 0.0090 mole, 91%, m.p: 274-276°C, lit : m.p:274.5-275°C (19). This product had an activity of 675 μCi. IR: γ_{max} (KBr) cm^{-1} : 3436, 3036, 2960, 1565, 1465, 1435, 1395, 1348, 1279, 1203, 1145, 1087, 965, 946, 830, 759, 658, 626, 600. ^{1}H NMR: δ (DMSO-$_{D6}$) ppm: 6.03 (S, all protons). ^{13}C NMR: δ (DMSO-$_{D6}$) ppm: 67.2 (all carbons).

CONCLUSION

The synthesis of carbon-14 labelled HMX was performed successfully with high yield and chemical purity. In all cases, the IR and NMR spectroscopy of the ^{14}C-products were identical to the spectroscopy of known samples. ^{14}C-HMX was synthesized according to the DADN route using the nitric acid/phosphorus pentoxide system for the nitrolysis of DADN. Many routes were evaluated during this study with cold starting materials and the DADN procedure was considered to be the best method to synthesize radioactive HMX. It appeared that the nitric acid strength, the phosphorus pentoxide concentration and the temperature were very important parameters of the nitrolysis reaction. Best results and best yields were obtained using freshly distilled nitric acid 100%. The ^{14}C-HMX sample had a total activity of 675 μCi. The purity of all the products isolated in the syntheses was determined using IR and NMR spectroscopy.

ACKNOWLEDGMENTS

The National Research Council of Canada and the Department of National Defence are greatly acknowledged for their support of this project. The authors wish to thank Ms. Louise Paquette and Ms. Anka Mihoc for their help in assessing the radioactivity of the labelled HMX.

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