SYNTHESIS AND ISOTOPE-RATIO ANALYSIS OF METHYL NITRITE-^{15}N

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SUMMARY

Methyl nitrite-^{15}N was synthesised on a 0.1 mole scale by the esterification of methanol by aqueous $H^{15}NO_2$. The method is simple and efficient, and provides analytically pure $CH_3O^{15}NO$. A method for determining the ^{15}N enrichment of $CH_3O^{15}NO$ is described.

Key words: esterification, isotope-ratio analysis, methanol, methyl nitrite, ^{15}N, nitrous acid methyl ester.

INTRODUCTION

During the course of studies of the hydrolysis of methyl nitrite in soils [1] it became neccessary to synthesise $CH_3O^{15}NO$ in order to assess its chemical interaction with soil organic matter. These studies required moderate amounts (0.1 mole) of moderately enriched (5 to 10 atom % ^{15}N) isotope. Accurate isotope-ratio analysis of the $CH_3O^{15}NO$ was also required, in order to obtain quantitative data on its transformation to other forms of N within the soil.

Several stable isotopic species of methyl nitrite, including $CH_3O^{15}NO$, have been used in infrared and microwave spectral studies of the structure of its *cis*- and *trans*-isomers [2,3] and of the products of its photolysis [4]. Two different methods have been used to synthesise $CH_3O^{15}NO$ [2,4]. The method developed by Turner *et al.* [2] was based on the conversion of $H^{15}NO_3$ to ^{15}NO by reaction with excess sulphuric acid on mercury. Dinitrogen-$^{15}N_2$ trioxide was formed by

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oxidation of ^{15}NO with O_2 (molar ratio of 4 :1), and used to esterify methanol below 0°C to produce $CH_3O^{15}NO$. The sequence of reactions is represented by:

$$2\,H^{15}NO_3 + 6\,Hg + 3\,H_2SO_4 \longrightarrow 2\,^{15}NO + 3\,Hg_2SO_4 + 4\,H_2O$$

$$4\,^{15}NO + O_2 \longrightarrow 2\,^{15}N_2O_3$$

$$^{15}N_2O_3 + 2\,CH_3OH \longrightarrow 2\,CH_3O^{15}NO + H_2O$$

The method used by Müller *et al.* [4] to synthesise $CH_3O^{15}NO$ was based on a photochemical procedure developed by Geiger *et al.* [5], and involved exchange between CH_3ONO and an excess of commercially-available ^{15}NO, under irradiation at 365 nm. Under these conditions, CH_3ONO is dissociated into methoxyl radicals and NO, and the isotopic species is obtained via an exchange reaction according to:

$$CH_3ONO + {}^{15}NO \xrightarrow{h\nu} CH_3O^* + NO + {}^{15}NO$$

$$CH_3O^* + NO + {}^{15}NO \xrightarrow{h\nu} CH_3O^{15}NO + NO$$

The published methods [2,4] appeared to be particularly suited to small scale (10^{-3} mole) preparation of highly enriched (95-99.4 %) isotope. Because of perceived complexities in the procedures and difficulties of larger scale adaptation, an alternative method was sought to provide the quantities and enrichments of $CH_3O^{15}NO$ needed for our experiments. The efficacy of the classical method of synthesis (esterification of methanol with aqueous nitrous acid) was therefore investigated. The objective of this study was to develop a simple yet efficient procedure for the synthesis and isotope-ratio analysis of pure $CH_3O^{15}NO$.

EXPERIMENTAL

Synthesis of Methyl Nitrite-^{15}N

Methyl nitrite-^{15}N was synthesised by initially transferring 16 ml of 6 *M* H_2SO_4 to an amber 100 ml round bottom flask (short neck, Quickfit FR 100/1S) immersed in liquid N_2. After freezing (approximately 10 min), a solution containing 5 ml CH_3OH and 7.04 g $Na^{15}NO_2$ (5 to 10 atom % ^{15}N) dissolved in 10 ml H_2O was slowly added, and rinsed twice with 5 ml CH_3OH during transfer.

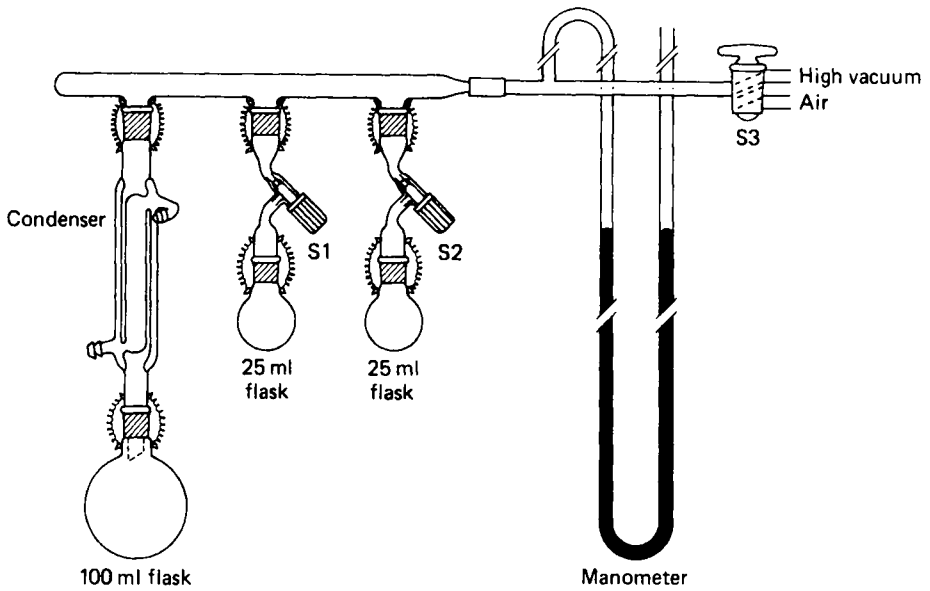

Figure 1. Distillation apparatus.

After freezing occurred (approximately 10 min), the flask was attached to the distillation apparatus (Figure 1), darkened by exposure to γ-irradiation, and mounted on a frame inside a fume cupboard.

After evacuating the apparatus to 7 x 10^{-3} kPa (S2 closed, S1 and S3 open to pump), the 25 ml flask attached to S1 was immersed in an alcohol-Dry Ice mixture and S3 closed. The 100 ml flask was then heated in a stream of warm air until the reaction commenced, and then allowed to proceed at room temperature until completion (effervescence ceased after 20-30 min). With S1 closed, the vacuum was released (S3 open to air), and the condenser and the 100 ml flask were removed and replaced with a 25 ml flask.

The apparatus was again evacuated (S2 and S3 open to pump) and, after closing S3, the freezing bath was transferred from the flask containing the $CH_3O^{15}NO$ to the flask attached to S2. After opening S1 the bulb-to-bulb distillation was allowed to proceed until completion. After closing S2, the vacuum was released, the empty flask removed from S1 and S1 closed. The bulb-to-bulb distillation procedure was then repeated to transfer the $CH_3O^{15}NO$ to the remaining empty 25 ml flask. On completion of distillation, the freezing bath was removed, and the flask containing $CH_3O^{15}NO$ detached when the pressure reached atmospheric. The flask was then stoppered with a No.29 suba-seal and the yield determined gravimetrically. The flask containing the $CH_3O^{15}NO$ was stored in the freezing bath until required.

Analytical

Duplicate samples (1.5 ml, 25°C) were taken with a gas-tight syringe before and after each distillation for the determination of analytical purity. The flask containing the $CH_3O^{15}NO$ was allowed to warm and positive pressure was released five times before a sample was taken for analysis. The purity was determined by analysis of N and -OCH_3 [6].

The isotopic composition of pure $CH_3O^{15}NO$ was determined by quantitative absorption of a sample (1.5 ml, 3 replicates) in acid $KMnO_4$ solution [6]. The $^{15}NO_3^-$ formed in solution was reduced to $^{15}NH_4^+$ by steam distillation [7], and the distillate prepared and oxidized by alkaline hypobromite to $^{15}N_2$ for isotope-ratio analysis using procedures described by Buresh *et al.* [8]. The m/e 28 : m/e 29 ratios were determined on a double collector, magnetic deflection (90° sector, 10 cm radius) AEI MS3 mass spectrometer. The isotopic composition of the $Na^{15}NO_2$ solution was determined by the same procedure following reduction of $^{15}NO_2^-$ to $^{15}NH_4^+$ by steam distillation [8].

RESULTS AND DISCUSSION

Two bulb-to-bulb distillations were required to obtain pure $CH_3O^{15}NO$ (Table 1), which is consistent with results obtained by Magalhães and Chalk [6] using a similar procedure to prepare CH_3ONO on a 1 mole scale. Low temperature vacuum distillation to separate $CH_3O^{15}NO$ was also used in other methods of synthesis [2,4]. The synthesis and purification procedures were very efficient, as illustrated by the high yield of pure compound obtained (Table 1). The yield was somewhat higher than the yield (90.7 %) obtained by synthesis of CH_3ONO on a larger scale [6]. The ^{15}N enrichment of pure $CH_3O^{15}NO$ did not differ significantly from that of the $Na^{15}NO_2$ precursor (Table 1), indicating the effectiveness of the procedure used for the isotope-ratio analysis of $CH_3O^{15}NO$.

The synthesis of $CH_3O^{15}NO$ by means of a single reaction is the principal advantage of the proposed method, as represented by:

$$2\,CH_3OH + 2\,Na^{15}NO_2 + H_2SO_4 \xrightarrow{aqu.} 2\,CH_3O^{15}NO + Na_2SO_4 + 2\,H_2O$$

The method proposed by Müller *et al.* [4] requires pre-synthesis of CH_3ONO before exchange with ^{15}NO. The efficiency of the method, as determined by the recovery of ^{15}N in the end-product,

Table 1. Recoveries of N and -OCH_3 in $CH_3O^{15}NO$ before and after distillation (1.5 ml, 25°C), and yield and isotopic composition of the pure compound.

Nº of distillations	Recovery[a](μeq) N	Recovery[a](μeq) -OCH_3	Yield[b] (g)	Atom % ^{15}N[c]
0	51.2 ± 0.1 (84.8)	51.1 ± 2.2 (84.7)		
1	59.2 ± 0.1 (98.1)	59.3 ± 1.2 (98.3)		
2	60.4 ± 0.2 (100.1)	60.2 ± 0.1 (99.8)	5.75 (94.2)	10.46 ± 0.04

[a] 1.5 ml of pure sample at 25°C theoretically contains 60.3 μeq N and -OCH_3. Data are means of duplicate determinations ± standard deviation. Data in parentheses are mean % purities.

[b] 0.1 mole CH_3ONO = 6.1 g. Value in parenthesis is % yield.

[c] Mean of 3 replicates ± standard deviation. Atom % ^{15}N of $Na^{15}NO_2$ precursor was 10.45 ± 0.02.

may also be lower than the classical method, because of the need for excess ^{15}NO, and the occurrence of the following side reactions:

$$CH_3ONO \xrightarrow{h\nu} H_2CO + HNO$$

$$2\,HNO \longrightarrow N_2O + H_2O$$

The principal advantage of the method described by Turner *et al.* [2] is its cost-effectiveness, since $H^{15}NO_3$ is used as the precursor, and the conversion of $H^{15}NO_3$ to ^{15}NO is almost quantitative [9].

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