PREPARATION OF METHYL NITRATE AND NITROMETHANE LABELLED WITH NITROGEN-15 AND OXYGEN-18,

SUMMARY

Methods are presented for the preparation on 10^{-3} mole scale of nitromethane and methyl nitrate enriched with oxygen-18 or nitrogen-15. Enrichment in each atomic position is discussed.

In the course of detailed studies[1,2] by microwave spectroscopy of the two molecules methyl nitrate[1] and nitromethane[2], aimed primarily at the determination of their detailed molecular geometry, it proved necessary to prepare small samples of these molecules enriched in each discrete atomic position with nitrogen-15 and oxygen-18. These enrichments have proved to be quite challenging, and it is with this in mind that we have decided to publish some aspects of this work in detail, in order to assist other workers engaged in similar work on related molecules.
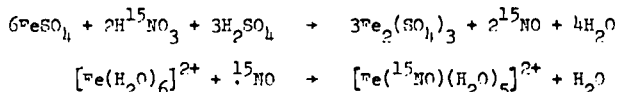
Our spectroscopic work was conducted at sample pressures of $1 - 10$ Nm^{-2} in an absorption cell and associated vacuum line ~ 2 litres in volume. The size of sample required, even for repeated dosing, was therefore fairly small ($\sim 10^{-4}$ mole). However, since work on this scale greatly increases preparative and sample handling problems, the present work has been conducted on 10^{-3} mole scale, this representing a compromise between isotope usage and preparative difficulty.

The work has depended considerably on three simple but efficient

reactions. The isotopic materials at our disposal were oxygen-18 gas (93% enriched) and $H^{15}NO_3$ (95% enriched) which, except in the preparation of $CH_3O^{15}NO_2$ by direct esterification[3] of c.p. methanol with $H^{15}NO_3$, required conversion into more suitable isotopic materials. The three methods used were:-

(1)   The "brown ring" reaction for conversion of $H^{15}NO_3$ into ^{15}NO:-

$$6FeSO_4 + 2H^{15}NO_3 + 3H_2SO_4 \rightarrow 3Fe_2(SO_4)_3 + 2^{15}NO + 4H_2O$$

$$[Fe(H_2O)_6]^{2+} + {}^{15}NO \rightarrow [Fe(^{15}NO)(H_2O)_5]^{2+} + H_2O$$

Ferrous ammonium sulphate rather than ferrous sulphate was used in this reaction, according to the method for determination of nitrate given by Vogel[4]. $H^{15}NO_3$ (~ 0.4 g) was distilled under vacuum into ~ 60 ml of ferrous/sulphuric acid mixture contained in a 150 ml flask. ^{15}NO (~ 6 mmoles) was removed from the mixture under vacuum by gentle warming.

(2)   Conversion of nitric oxide into nitrogen dioxide:-

$$2NO + O_2 \rightarrow 2NO_2$$

In different circumstances this reaction could be used for either nitrogen-15 or oxygen-18 enrichment. Where a 100% excess of NO was used, enriched N_2O_3 was prepared. This reaction was conveniently conducted on 10^{-3} mole scale by allowing the gases to mix in the manifold (~ 55 ml) of a simple vacuum system incorporating a mercury manometer.

(3)   The oxidation of metallic sodium, and subsequent hydrolysis:-

$$2Na + {}^{18}_{2}O_2 \rightarrow Na_2^{18}O \xrightarrow{H_2^{16}O} Na^{18}OH + Na^{16}OH$$
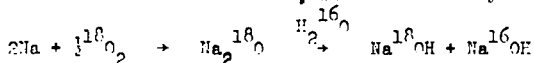
A sodium pellet (0.023 g) was melted by gentle heating under vacuum and allowed to react with oxygen-18 gas, any excess sodium being hydrolysed in the second stage. Water (0.018 g) was weighed and
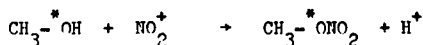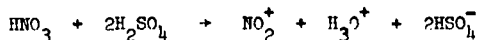
condensed onto the sodium oxide under vacuum.

Preparation of the two $CH_3ON^{16}O^{18}O$ species was achieved using $^{18}O_2$ in reaction (2), followed by hydrolysis of the $N^{16}O^{18}O$ in the presence of the stoichiometric quantity of oxygen for the reaction:-

$$2N^{16}O^{18}O \; + \; \frac{1}{2}^{16}O_2 \; + \; H_2^{16}O \; \rightarrow \; 2HN^{16}O_2^{18}O$$
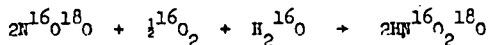
The enriched nitric acid produced was then used in the direct esterification[3] of c.p. methanol in the presence of concentrated sulphuric acid. The overall oxygen-18 enrichment was ~20%. Two drops of methyl nitrate were formed as an oil on the surface of the aqueous solution facilitating separation by distillation.

The above synthesis failed to yield any microwave spectral features attributable to $CH_3^{18}ONO_2$, this result being explicable in terms of the accepted[5] mechanism for the esterification reaction, i.e.
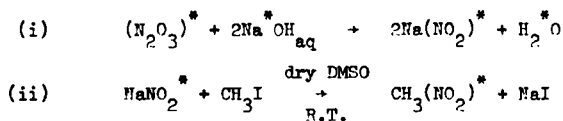
$$HNO_3 \; + \; 2H_2SO_4 \; \rightarrow \; NO_2^+ \; + \; H_3O^+ \; + \; 2HSO_4^-$$

$$CH_3-\overset{*}{O}H \; + \; NO_2^+ \; \rightarrow \; CH_3-\overset{*}{O}NO_2 \; + \; H^+$$

The synthesis of $CH_3^{18}ONO_2$ therefore required a sample of ^{18}O-enriched methanol. This was prepared by the reaction[6]:-

$$Na^{16,18}OH_{aq} \; + \; CH_3I \; \xrightarrow[\text{sealed tube}]{90^\circ C} \; CH_3^{16,18}OH \; + \; NaI$$
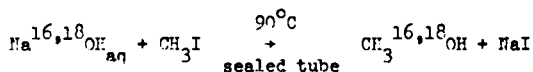
using sodium hydroxide prepared by reaction (3). Methyl iodide (10^{-3} mole) was distilled into a Carius tube (10 cm x 1 cm) containing water (10^{-3} mole) and sodium hydroxide (10^{-3} mole). The contents were sealed under vacuum and heated at $90^\circ C$ for five days. Residual methyl iodide was pumped off at $-78^\circ C$ and the methyl alcohol distilled into the nitration mixture.

The enrichment procedures for $CH_3^{15}NO_2$ and $CH_3N^{18}O^{16}O$ had a common reaction sequence:-

(i) $(N_2O_3)^* + 2Na^*OH_{aq} \rightarrow 2Na(NO_2)^* + H_2^*O$

(ii) $NaNO_2^* + CH_3I \xrightarrow[R.T.]{dry\ DMSO} CH_3(NO_2)^* + NaI$

where the asterisk indicates isotopic enrichment, and the dinitrogen
trioxide and sodium hydroxide were prepared using reactions (2) and
(3) above. The second stage of this sequence has been studied by
Kornblum et al[7,8] and yields of 50-60% have been obtained using DMF
or DMSO as solvent. Here the more involatile DMSO was used to
facilitate removal of the nitromethane product by distillation. Despite
the poor solubility of sodium nitrite in DMSO, good yields of nitro-
methane were obtained with reaction times of about 30 minutes, using
10^{-3} mole quantities of reactants and ~ 0.5 cm^3 of DMSO (dried over
calcium hydride). The nitromethane product tended to contain some
minor impurities, such as methyl iodide, which were difficult to
remove completely on this scale.

   Two problems were encountered in connection with reaction (i)
above. In order to optimise oxygen-18 usage a minimum of excess
water was preferred; however, at high sodium hydroxide concentrations
the reaction was found to be very inefficient, producing nitrate
rather than nitrite ion with evolution of nitric oxide. For the
oxygen-18 enrichment, therefore, a minimum of excess water was
determined such that both nitrite yield and oxygen-18 enrichment level
were satisfactory; this corresponded to a 40 mole per cent solution
of sodium hydroxide, leading to an oxygen-18 enrichment level of
$\sim 20\%$ in nitromethane. For the nitrogen-15 enrichment this consideration
did not apply, and a more dilute solution of sodium hydroxide was used,
giving a higher nitrite yield.

   A second difficulty arose from unreacted sodium hydroxide from
reaction (1), which if carried over into reaction (ii) tended to

destroy the nitromethane yield with the formation of a yellow product. This difficulty was eliminated by neutralising the excess alkali by the addition of carbon dioxide, prior to removal of excess water from the nitrite reaction.

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