THE SYNTHESIS OF ^{18}O MULTILABELED ANHYDROUS NITRIC ACID

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SUMMARY

^{18}O-multilabeled anhydrous nitric acid (89 atom % ^{18}O) was prepared by exchange with $H_2{}^{18}O$, neutralization with NH_3, and distillation from methane sulfonic acid. The use of trifluoromethane sulfonic acid, sulfuric acid, and oleum was also investigated, but these acids were found unsuitable due to rapid oxygen exchange. The extent of exchange was monitored by converting water to methanol, nitric acid to nitroanisole, and analyzing by field ionization mass spectrometry.

A study undertaken to measure the room temperature vapor pressures of explosives by isotope dilution techniques [1] using nonfragmenting field ionization mass spectrometry (FIMS) [2] required the preparation of ^{18}O-multilabeled anhydrous nitric acid for the synthesis of stable isotope multilabeled ethylene glycol dinitrate, nitroglycerin, and pentaerythritol tetranitrate. A high extent of labeling was required to maximize the dynamic range of the dilution analysis by minimizing interferences

between labeled and unlabeled compounds.[2] In spite of its apparent simplicity, no procedure for the preparation of isotopically labeled anhydrous nitric acid has been reported. Because this material may be useful in many synthetic procedures, we have decided to describe its preparation in this communication.

The general approach to the preparation of $HN^{18}O_3$ was to exchange nitric acid with $H_2{}^{18}O$,[3] neutralize with ammonia, distill off the exchanged water, dissolve the $NH_4N^{18}O_3$ in a strong acid, and distill off the anhydrous $HN^{18}O_3$. An initial synthesis by this scheme, in which the labeled nitric acid was distilled from oleum, resulted in a product which was unexpectedly low in ^{18}O (39 atom % ^{18}O vs. a predicted 80%). Evidently there was a fairly rapid oxygen exchange between the nitric acid and the SO_3-sulfuric acid solvent.

We then determined the extent of oxygen exchange with four different acids. It was first necessary to develop a fast and reliable method for measuring the isotopic abundance of ^{18}O in the nitric acid and in the water. Nitric acid could not be analyzed <u>per se</u> because of its chemical reactivity, and ammonium nitrate also could not be analyzed <u>per se</u> by the mass spectrometer because of its thermal instability. Molecular water could not be analyzed directly because of the H_2O background in the spectrometer vacuum system. The ^{18}O abundance in the nitrate was determined by dissolving the $NH_4N^{18}O_3$ in methane sulfonic acid and adding a solution of anisole in methylene chloride to produce nitroanisole, which could be easily handled by the mass spectrometer. Determination of the relative abundances of the parent ion mass peaks 153 ($-NO_2$), 155 ($-N^{18}O^{18}O$), and 157 ($-N^{18}O_2$) allowed calculation of the extent of oxygen exchange. The isotopic abundance in the water was determined by reacting

the water with dimethyl sulfate and measuring the ratio of masses 32/34 of the methanol product. The much lower ionization efficiency of O_2 by field ionization compared with that of MeOH eliminates the potential interference of residual O_2 in the mass spectrometer. The MeOH method for H_2O isotopic analysis is preferred over the CO_2 equilibration procedure, which is inadequate at high ^{18}O concentrations, and over the more complicated NaOBr method.[4]

The rate of oxygen exchange was then determined under anhydrous conditions between nitric acid and methane sulfonic acid (Eastman), trifluoromethane sulfonic acid ("Trimsyl," 3M), sulfuric acid and oleum. The $NH_4N^{18}O_3$ (39 atom % ^{18}O) was dissolved in the acid (10- to 20-fold excess in oxygen), allowed to exchange, converted to nitroanisole, and the decrease in ^{18}O content determined. For freshly distilled methane sulfonic acid the exchange was quite slow, thus validating the analytical method described above. After one hour at 37°C the ^{18}O label had diminished from 39.4% to 38.7% -- within measurement error. After 14 hr at 37° it was 27%. In trifluoromethane sulfonic acid at room temperature the ^{18}O label decreased to 27% in 15 min. In oleum the ^{18}O content declined to 23% immediately (in the time it took to dissolve the $NH_4N^{18}O_3$ and convert to nitroanisole--about 5 min). The most rapid exchange was in H_2SO_4; ^{18}O content fell to 10% immediately and to 2% (complete exchange) in 30 min at room temperature. The presence of water in the sulfuric acid probably served to accelerate the exchange process. Thus, methane sulfonic acid was clearly the reagent of choice for the synthesis of $HN^{18}O_3$.

The equilibria: $H_2SO_4 \rightleftarrows H_2O + SO_3$

$$HNO_3 + H_2SO_4 \rightleftarrows HSO_4^- + H_2NO_3^+$$

$$H_2NO_3^+ \rightleftarrows H_2O + NO_2^+$$

may have contributed to the isotopic exchange in sulfuric acid and oleum. CH_3SO_3H, on the other hand, cannot readily undergo spontaneous "monomolecular" dehydration.

We then proceeded with the synthesis of $HN^{18}O_3$ by the following route. $HN^{18}O_3$ (7.6 g, 39 atom % ^{18}O) was obtained by vacuum distillation of the initial batch of labeled NH_4NO_3 from 30 ml of freshly distilled methane sulfonic acid. The $HN^{18}O_3$ was then allowed to exchange with 13 ml of $H_2{}^{18}O$ (95 atom % ^{18}O) obtained from Monsanto's Mound Laboratory. The proportions were chosen so as to maximize oxygen transfer to the nitric acid while allowing a reasonable rate of exchange. The exchange was carried out at 75° to minimize thermal decomposition of HNO_3. At this temperature and concentration the $t_{\frac{1}{2}}$ for exchange was calculated to be $\sim$ 33 hr, based on the kinetic data of Anbar and Guttman.[3] Progress of the exchange was followed by periodically removing 0.05 ml aliquots, neutralizing with NH_3, pumping off water, converting to nitroanisole and analyzing by FIMS. After 6 days the nitric acid was 75 atom % ^{18}O labeled. This was neutralized with NH_3, the water removed by vacuum distillation, the $NH_4N^{18}O_3$ dissolved in methane sulfonic acid, and the $HN^{18}O_3$ distilled into a liquid nitrogen trap under vacuum. The yield was 5.7 g anhydrous $HN^{18}O_3$ (75 atom % ^{18}O).

This nitric acid was then subjected to a second exchange with 13 ml of $H_2{}^{18}O$ (98 atom % ^{18}O) for 14 days. The exchange period was longer because of the lower HNO_3 concentration. The nitric acid was then recovered as above; the final yield was 4.3 g anhydrous $HN^{18}O_3$ (89 atom % ^{18}O); theoretical for complete exchange was 91.8 atom % ^{18}O.

The method described enables the synthesis of ^{18}O-multilabeled anhydrous nitric acid by exchange with $H_2{}^{18}O$, without loss of label in

the recovery of the acid from the aqueous medium.

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