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Preparation of Oxygen-18 Enriched Sulfur Trioxide

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Oxygen-18 enriched sulfur trioxide has been prepared by a simple and relatively inexpensive procedure. This has been accomplished by the addition of sulfur trioxide to oxygen-18 enriched water to form fuming sulfuric acid containing approximately 50 per cent dissolved sulfur trioxide. On distillation of this fuming sulfuric acid, the sulfur trioxide obtained was enriched in oxygen-18. It was isolated and analyzed as its dimethylformamide complex.

LA PREPARATION DU TRIOXYDE DE SOUFRE ENRICHI D'OXYGÈNE-18

On a préparé du trioxyde de soufre enrichi d'oxygène-18 par un procédé simple et rélativement peu coûteux. Ceci on a achevé en ajoutant du trioxyde de soufre à de l'eau enrichie d'oxygène-18 pour former de l'acide sulfurique fumant contenant environ 50 pour cent de trioxyde de soufre en solution. Lors de la distillation de cet acide sulfurique fumant, le trioxyde de soufre que l'on obtint fut enrichi d'oxygène-18. Ceci fut isolé et analysé sous la forme de son complexe de diméthylformamide.

ПРИГОТОВЛЕНИЕ ТРЕХОКИСИ СЕРЫ, ОБОГАЩЕННОЙ КИСЛОРОДОМ-18

Описан простой, относительно недорогой метод приготовления трехокиси серы, обогащенной O^{18}. Добавление трехокиси серы к воде, обогащенной O^{18}, дает дымающая серная кислота, содержащая приближенно 50% растворенной трехокиси серы. При дистилляции этой дымающей серной кислоты получается трехокись серы, обогащенной O^{18}. Выделение и анализ—в виде комплекса диметилформамида.

ZUBEREITUNG VON ^{18}O ANGEREICHERTEM SCHWEFELTRIOXYD

^{18}O angereichertes Schwefeltrioxyd ist in einem einfachen und verhältnismässig billigen Verfahren hergestellt worden. Man erreichte das durch die Zugabe von Schwefeltrioxyd zu ^{18}O angereichertem Wasser zur Bildung rauchender Schwefelsäure mit einem Gehalt von etwa 50% gelöstem Schwefeltrioxyd. Bei der Destillation dieser rauchenden Schwefelsäure war das erhaltene Schwefeltrioxyd mit ^{18}O angereichert. Es wurde getrennt und analysiert als sein Dimethylformamid-Komplex.

INTRODUCTION

It was desired to obtain a small quantity of oxygen-18 enriched sulfur trioxide for mechanistic studies. However, the usual method[1] of preparing sulfur trioxide by the oxidation of sulfur dioxide over vanadium pentoxide is inefficient and would be costly if oxygen gas enriched in oxygen-18 were employed.

The preparation described herein relies upon the highly ionized state of concentrated sulfuric acid, as shown in equation (1).

$$2H_2SO_4 \underset{K_2}{\overset{K_1}{\rightleftharpoons}} SO_3 + H_3O^+ + HSO_4^- \quad (1)$$

where $K_1 \simeq 4 \times 10^{-1}$ and $K_2 \simeq 1.2 \times 10^{-2}$ at 25°C.[2]

By allowing pure unenriched sulfur trioxide to react with oxygen-18 enriched water in equal molar quantities, oxygen-18 enriched sulfuric acid is produced. An excess of unenriched sulfur trioxide is then added to give approximately 50% fuming sulfuric acid, which, on equilibrium, yields enriched sulfur trioxide that can be stored as fuming sulfuric acid and distilled off prior to use.

When 30% oxygen-18 enriched water was employed with this procedure, the percentage

of oxygen-18 in the sulfur trioxide was increased from the naturally occurring abundance of 0.20% to 3.58% with the $S^{16}O_2{}^{18}O/S^{16}O_3$ abundance ratio equal to 10.74%. It should be possible to achieve a higher enrichment by starting with water containing a higher percentage of oxygen-18 or by recycling the oxygen-18 enriched sulfur trioxide from the initial reaction through several subsequent reactions with water of the same percentage enrichment.

EXPERIMENTAL

Preparation of fuming sulfuric acid

Since the reaction between water and sulfur trioxide is highly exothermic, the addition must be done with extreme care to avoid spattering. 10 ml of liquid sulfur trioxide were placed in a 300-ml two-neck flask equipped with an electric mantle and heated to 125°C. Dry nitrogen was passed through the flask at 15 ml/min. This stream was passed into a two-neck 10-ml flask equipped with a drying tube. This flask contained 1 ml (0.96 g) of the 30% oxygen-18 enriched water and was kept at 0–5°C with an ice bath.

The passage of sulfur trioxide vapor into the enriched water was continued for 55 min after which time a white solid (H_2SO_4) began to form in the cooled flask. The ice bath was removed and the solid went into solution. Liquid sulfur trioxide was then added to this solution at room temperature until a total of 6.64 g of sulfur trioxide had been added to yield 54.2% fuming sulfuric acid. Therefore, 2.55 g (0.032 *M*) of dissolved sulfur trioxide is available for subsequent use.

Preparation of the dimethylformamide sulfur trioxide complex

Since it is not convenient to determine the enrichment of the oxygen-18 in the sulfur trioxide directly, its dimethylformamide complex[3] was prepared, from which the enrichment was determined by mass spectrometry.

Dimethylformamide (2.2 g, 0.032 *M*) was dissolved in 35 ml of ethylene dichloride at room temperature in a 50-ml round-bottom flask equipped with a magnetic stirrer. Since the dimethylformamide-sulfur trioxide complex is insoluble in this solvent, it is necessary to incorporate a sliding glass rod into the delivery tube of the reaction flask to clear the solid complex that might clog the tube.

The flask containing the 54.2% fuming sulfuric acid was connected to the receiver containing the dimethylformamide and the fuming sulfuric acid heated to 125° to distill over the sulfur trioxide. The solid white complex came out of solution and periodically the delivery tube was cleared by pushing the solid complex into the solvent. The reaction was stopped after passing sulfur trioxide vapor into the reaction flask for 2 hr. The solid complex was filtered rapidly and washed several times with fresh ethylene dichloride. The complex (78% yield) was then stored under nitrogen at 0°. This material was analyzed on a CEC Model 21-491 mass spectrometer with a solids probe at 70° for the $^{18}O/^{16}O$ abundance ratio. This gave an average of 3.58% ± 0.16% oxygen-18 enrichment for the four samples examined. Further examination indicated that no oxygen-18 enrichment of the dimethylformamide carbonyl took place in the complex.

REFERENCES

1. Davies P. British Patent 895,624 (1962).
2. *A Condensed Laboratory Handbook*, p. 14. Du Pont de Nemours (1965).
3. Kenner G. W. U. S. Patent 2,766,225 (1956).