| Experiment | 1 | 2 |
|---|---|---|
| Tetraacetyl-L-arabonic acid nitrile, moles | 1 | 1 |
| Normal acetamide in solution, moles | 4 | 8 |
| Excess of $N^{15}$ in ammonia employed | 6.2 | 6.2 |
| Excess of $N^{15}$ in L-erythrose diacetamide formed | 5.69 | 5.71 |

In a control experiment, 100 mg. of acetamide was dissolved in ethanolic ammonia in which 6.2 atom per cent. excess of $N^{15}$ was present. After forty-eight hours, evaporation of the ethanol yielded acetamide containing no $N^{15}$. From this it is evident that no detectable exchange of normal nitrogen and $N^{15}$ took place under the conditions used.

These experiments suggest that "aldose diacetamides" do not arise from condensation of preformed acetamide with any sugar derivative, since if this occurred a larger proportion of $N^{14}$ would be expected in the product, especially as the proportion of acetamide is increased in the environment (as in the second experiment). On the other hand an intramolecular mechanism such as that suggested by Isbell and Frush provides a simple explanation of the observations.

It will be noted that a small proportion of normal ammonia may be formed by hydrolysis of cyanide. The presence of a little normal ammonia could explain the slight dilution of $N^{15}$-rich ammonia that appears to have occurred, though this is scarcely greater than the experimental error.

Further experiments are in progress.

We wish to acknowledge our indebtedness to Dr. David Rittenberg and Miss Laura Ponticorvo of the Columbia University College of Physicians and Surgeons, Department of Biochemistry, for mass spectrometer determinations of $N^{15}$.

SUGAR RESEARCH FOUNDATION, INC.
NEW YORK, N. Y.
LABORATORIO DE QUIMICA ORGANICA
FACULTAD DE CIENCIAS EXACTAS, FISICAS Y NATURALES
BUENOS AIRES, ARGENTINA
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## Preparation of Radioactive Sulfur Dioxide from Barium Sulfate[1]

BY ROWLAND E. JOHNSON AND J. L. HUSTON

There has been a need in this Laboratory for a simple and direct method for making radioactive sulfur dioxide from barium sulfate. At the present time the only method which has been used to convert radioactive barium sulfate to a chemically more useful form has been reduction at 900–1000° with carbon or hydrogen. This process has been carefully studied by Wells,[2] who has shown that good yields of barium sulfide (better than 90%) are obtained if the barium sulfate is heated rapidly to high temperatures. This precaution has not been observed by all workers.

One can then generate hydrogen sulfide from the barium sulfide, oxidize this to sulfur with triiodide solution,[3,4] and burn the sulfur after filtration of the resulting suspension. Apart from being tedious and indirect, this procedure is somewhat objectionable since sulfur dioxide prepared by combustion of sulfur is always contaminated by some sulfur trioxide which usually must be removed by an appropriate washing process. We find that combustion in oxygen of an intimate mixture of barium sulfate and red phosphorus gives a good yield of pure sulfur dioxide. Combustion in air gives poor yields.

The combustion was effected by means of a gas train consisting of the following: (1) drying tubes containing calcium chloride and "Caroxite" (a carbon dioxide absorbent), (2) a mercury blow-off valve, (3) a flow meter of the differential manometer type, (4) a combustion flask, (5) a tube containing glass wool to filter phosphorus pentoxide from the gas stream, (6) two glass spirals cooled with liquid oxygen, and (7) an aspirator. The combustion flask was made from a 1-liter filter flask by sealing on a short piece of tubing tangential to the bottom and was fitted at the top with a two-hole stopper carrying leads which terminated in a short length of resistance wire for ignition of the charge. The bottom of the flask was covered with a protective layer of clean sand prior to insertion, through the lower inlet, of an alundum boat containing the charge. The first of the two spirals (6), was of conventional design, but the second contained a plug of glass wool in a large (2 cm. o.d.) central tube to assure complete removal of sulfur dioxide from the gas stream. Most of the sulfur dioxide freezes as a loose powder which can easily undergo mechanical transfer beyond the refrigerated region; in practice the omission of the glass wool plug resulted in about 5% loss.

With a stream of oxygen passing through the lower tube of the combustion flask and out the upper side arm, the resistance wire was brought into contact with the charge and the charge ignited by passing a momentary current through the wire. Combustion is completed in less than thirty seconds. A one-liter container is sufficiently large that the flame will not come in contact with glass. The residue from the combustion is a metaphosphate glass containing unreacted barium sulfate.

It should be noted that if liquid air or liquid nitrogen instead of liquid oxygen were to be used as a refrigerant, it would be desirable that a manometer be attached to the gas train near the spirals, so that the oxygen pressure might be adjusted sufficiently low (15 cm. for liquid nitrogen, about 35 cm. for liquid air) to prevent condensation.

After sulfur dioxide had been collected in the

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[1] Published with the approval of the Oregon State College Monographs Committee, Research Paper No. 147, Department of Chemistry, School of Science.

[2] A. E. Wells, *J. Ind. Eng. Chem.*, **8**, 770 (1916).

[3] R. A. Cooley and D. M. Yost, THIS JOURNAL, **62**, 2474 (1940).

[4] G. L. Clark, S. G. Gallo and B. H. Lincoln, *J. Applied Phys.*, **14**, 428 (1943).

spirals, it was transferred to a known volume for measurement of pressure and yield. Purity of the sulfur dioxide was verified by measurement of its vapor pressure at Dry Ice temperature.

Sample data are listed in Table I. It will be seen that while the yield is somewhat erratic, it is not greatly sensitive to variations in the experimental conditions. Accordingly, it is recommended that barium sulfate be mixed with at least its own weight of red phosphorus, and that the flow meter be dispensed with.

TABLE I

| Wt. $BaSO_4$, mg. | Wt. P/wt. $BaSO_4$ | Flow l./sec. $\times 10^2$ | Yield, % |
|---|---|---|---|
| 586 | 1.63 | 6.2 | 97 |
| 585 | 1.63 | 6.2 | 87 |
| 590 | 1.63 | 3.5 | 90 |
| 586 | 1.63 | 3.5 | 86 |
| 585 | 1.63 | 13.4 | 92 |
| 194 | 1.63 | 6.2 | 90 |
| 193 | 1.63 | 6.2 | 87 |
| 630 | 0.81 | 6.2 | 90 |
| 585 | 0.40 | 6.2 | 70 |
| 580 | 0.40 | 6.2 | 74 |

Sulfur dioxide, prepared by this method from radioactive barium sulfate, was examined for sulfur trioxide impurity by means of an apparatus which consisted essentially of two small flasks connected to each other, through a stopcock, by means of ground joints, with another stopcock and ground joint to permit connection to a vacuum line for evacuation and introduction of sulfur dioxide. Prior to evacuation, dilute hydrochloric acid was placed in one of the flasks and sodium hydroxide solution in the other. The liquids were frozen, the apparatus evacuated, and the stopcock connecting the two flasks was then closed. The sulfur dioxide was distilled onto the hydrochloric acid solution by means of liquid air, and the other stopcock closed. The apparatus was then removed from the vacuum line and the liquids allowed to melt. The stopcock connecting the flasks was opened and then, by cooling of the sodium hydroxide solution with a Dry Ice-bath, the solution of sulfur dioxide was vacuum distilled almost to dryness. The apparatus was taken apart, bromine water was added to the sulfite solution, sodium sulfate carrier added to both flasks, and the contents of the two flasks precipitated as barium sulfate. Radioactivities of the precipitates were determined in a manner which did not differ greatly from a method used previously for radiocarbon.[5] The results showed that the sulfur dioxide contained less than 0.1% of sulfur trioxide. The procedure, permitting rigorous exclusion of oxygen was preferable for our purposes to more standard titrimetric methods for analysis of sulfurous acid solutions. These are usually somewhat inaccurate due to air oxidation of sulfurous acid.

The radiosulfur was obtained carrier free (in potassium chloride) from the Atomic Energy Commission.

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[5] P. E. Yankwich, G. K. Rollefson and T. H. Norris, *J. Chem. Phys.*, **14**, 131 (1946).

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## The Density of Solutions of Alkali Metals in Liquid Ammonia

BY WARREN C. JOHNSON, ALBERT W. MEYER AND ROBERT D. MARTENS

Recent interest in the apparent molar volume of sodium in liquid ammonia[1,2] has prompted the writers to submit some data pertaining to lithium, sodium, and potassium solutions which were acquired a number of years ago, with the thought that they might be of assistance in the formulation of better theoretical concepts for these unusual solutions.

The procedure used for the determination of the density of solutions was essentially the same as that described by Kraus, Carney and Johnson[3] and Johnson and Meyer.[4]

The data for lithium solutions are given in Table I.

TABLE I

THE DENSITY OF SOLUTIONS OF LITHIUM IN LIQUID AMMONIA AT −33.2°

| Li, g. | $NH_3$, g. | Mole fraction Li | Density |
|---|---|---|---|
| 0.2291 | 16.476 | 0.0331 | 0.639 |
| .5545 | 22.452 | .0571 | .611 |
| .5053 | 16.030 | .0713 | .597 |
| .9170 | 16.813 | .1180 | .554 |
| .9170 | 12.199 | .1557 | .523 |
| 1.0697 | 13.621 | .1616 | .518 |
| 0.9170 | 9.241 | .1958 | .498 |
| 1.0697 | 8.895 | .2105[a] | .490 |

[a] Saturated solution, as determined by Johnson and Piskur, *J. Phys. Chem.*, **37**, 93 (1933).

An interpolation between Jaffe's two values for the saturated solution at −33° gives a value of 0.486 for the density[5]: this is in good agreement with our value of 0.490. The plot of mole fraction of lithium *versus* density gives a smooth curve and at zero mole fraction it intercepts the density axis at the density of pure liquid ammonia at −33.2°.[6]

The difference in volume, $\Delta V$, per mole of solute, between the volume of the solution and the sum of the volume of its components, when plotted against the dilution (moles of ammonia per mole of lithium) gives a curve very similar to those obtained from comparable plots for sodium and potassium solutions.[3,4] The curve passes through a maximum at a $\Delta V$ value of about 46 cc. This volume change is greater than that for either so-

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[1] Ogg, THIS JOURNAL, **68**, 155 (1946); *J. Chem. Phys.*, **14**, 114, 295, 399 (1946); *Phys. Rev.*, **69**, 668 (1946).

[2] Stosick and Hunt, THIS JOURNAL, **70**, 2826 (1948).

[3] Kraus, Carney and Johnson, *ibid.*, **49**, 2206 (1927).

[4] Johnson and Meyer, *ibid.*, **54**, 3621 (1932).

[5] Jaffe, *Z. Physik*, **93**, 741 (1935).

[6] Cragoe and Harper, *Bur. Standards Sci. Papers*, **420**, 313 (1921).