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A New Method of Preparing Nitric Oxide

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A new method of preparing nitric oxide which involves heating to a temperature slightly above 300° a dry powdered mixture of potassium nitrite and nitrate, chromic oxide and ferric oxide has been perfected. The nitric oxide so produced contained only a fraction of a per cent. of impurity.

Introduction

The production of common gases by heating a dry powder in a "Pyrex" sidearm of a vacuum system is rewarded with a great simplification of apparatus and manipulative technique. Some preparative examples are chlorine from cupric chloride, oxygen from potassium permanganate, nitrogen from sodium azide, and hydrogen sulfide from the commercial product "Aich-tu-ess." The authors have perfected a method for similarly preparing nitric oxide involving the stoichiometric equation

$$3KNO_2(l) + KNO_3(l) + Cr_2O_3(c) = 2K_2CrO_4(l \;\&\; c) + 4NO(g)$$

Experimental

In practice, a mixture of the proportions given by the above equation gives a melt which bubbles and spatters. It was found that this difficulty could be overcome by admixture of ferric oxide which had been calcined at 950° to remove water of hydration.

It was found advisable to calcine the chromic oxide at 950° to remove higher oxides and water.

The potassium nitrite thus far available as an article of commerce is not of sufficient purity to be weighed as such, but usually contains about 10% potassium nitrate. Material used by the authors was prepared by the addition of a solution of potassium chloride to a stirred aqueous suspension of silver nitrite in such a manner as to always have some dissolved silver nitrite in solution.

A mixture of the following proportions was found to represent the optimum in chemical reactivity and physical properties: 63.75 g. (0.750 mole) potassium nitrite, 25.25 g. (0.250 mole) potassium nitrate, 76 g. (0.50 mole) chromic oxide and 120 g. (0.752 mole) ferric oxide. The amount of chromic oxide is double that required for the reaction, but the use of a smaller amount gave incomplete evolution of nitric oxide.

The proportions of the components given above are such that if sufficient water is added to make a stiff paste, the material can be moulded into cylindrical pieces of about 1 inch diameter and allowed to dry. In this form the pieces retain their shape during and after nitric oxide evolution.

Pellets can be formed quite easily from the material in a small hand press. The extreme softness of the potassium nitrite allows it to act as a binder.

The slight hygroscopicity of potassium nitrite makes it necessary to predry the mixture at 100° if moisture free nitric oxide is required.

A ten-gram sample of the above mixture was placed in a "Pyrex" test-tube fitted with a rubber stopper having two outlets, the one leading to a graduate cylinder filled with dilute sodium hydroxide solution inverted in a pneumatic trough, the other leading to supplies of nitrogen and nitric oxide for flushing the generator prior to gas evolution. The test-tube after flushing was then heated with the yellow flame of a glass blowing torch (a hotter flame is not necessary) until no more gas would evolve to displace caustic solution from the graduate cylinder. A total of 872 cc. of gas at 25° and one atmosphere (corrected for water vapor) was collected, in good agreement with 868 cc. calculated. Oxygen prepared from sodium peroxide was then slowly bubbled into the graduate cylinder so as to form nitrite and nitrate from the nitric oxide. The "end-point" was approached very slowly so as to establish that 2 cc. of gas could not be caused to form nitrite and nitrate. The nitric oxide may thus be deduced to be 99.78% pure.

Reabsorption of evolved nitric oxide by the system is extremely slow so that there is no danger of sucking back water when evolving into a water displacement apparatus.

The spent sample was extracted with water to confirm the nature of the other product. The theoretical weight of yellow potassium chromate containing a trace of dichromate was obtained on evaporating the filtrate.

Similar experiments were carried out involving samples prepared with smaller molar ratios of potassium nitrate to nitrite. The gas collected contained increasing amounts of nitrogen and nitrous oxide in proportion to the lowering ratio of nitrate content. Material containing no potassium nitrate reacted to give about 7% nitrogen and 15% nitrous oxide. The latter was determined by infrared analysis of the gas, the nitrogen by difference.

In order to determine the temperature at which the pressure of the system approximates one atmosphere, a sample of correct proportions was placed in a "Pyrex" vacuum system equipped with a "Pyrex" Bourdon gage and a furnace surrounding the sample. A thermocouple was imbedded in the sample. At 310° a pressure of 760 mm. was developed. On maintaining the temperature constant at 310° for two days, no change in pressure was observed, thus the nitrous oxide and nitrogen formed when nitrate deficient samples were pyrolyzed was not due to catalytic decomposition of the nitric oxide gas.

The enthalpy for the reaction at room temperature calculated from data given by Rossini, *et al.*,[1] is 77.9 kcal. (endothermic). Thus, the mixture is quite stable, and no violent reaction is to be expected on heating it.

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(1) F. D. Rossini, D. D. Wagman, W. H. Evans, S. Levine and I. Jaffe, Natl. Bur. Standards Circ. 500 (1952).