

THE GAS ANALYSIS OF TRITIUM IN THE FORM OF ETHANE

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A new procedure for the determination of extremely low concentrations of tritium in atmospheric humidity is described, consisting in hydrogenation of acetylene to ethane. Hydrogen is prepared by reduction of tritium oxide contained in air humidity.

At present the proportional counters represent the most sensitive detectors for measuring very low tritium activities. Selecting the method of the preparation of the convenient gas filling containing atmospheric tritium we had to consider two points of view: the suitability of the gas for the filling of the proportional counter and the procedure of the preparation of the gas itself.

Owing to the fact that water is the most frequently coming form where the tritium concentration is to determine the reduction of water is the first step of the preparation of the counter gas filling. The mixture of hydrogen with a small amount of methane is used as a gas filling very seldom.

The sensitivity increase can be achieved with the hydrocarbon gas filling where one molecule of the gas contains more hydrogen atoms. The synthesis of methane from CO_2 and H_2 using

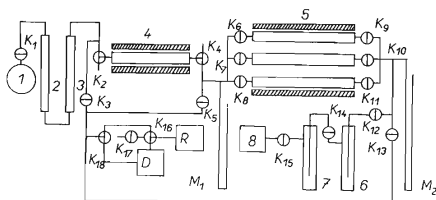


FIG. 1

Diagram of Apparatus for Desorption of Air Humidity

1 Bulb with Ar, 2, 3 absorption tubes, 4 furnace for the Ar purification, 5 furnace, 6, 7 traps, 8 flowmeter, R rotary pump, D diffusion pump, M_1 and M_2 manometers, K_1 — K_{17} vacuum stopcocks.

ruthenium as a catalyst is the time consuming work and it may also be a source of the isotopic fractionation¹. The other methods are based on the hydrogenation of the unsaturated hydrocarbons as *e.g.* acetylene, ethylene, propylene, butylene^{2,3} *etc.* Concerning some of these hydrocarbons several complications have to be born in mind, *e.g.* the difficulties with the preparation of the compounds in the sufficient purity, the possible reaction with the vacuum grease (propane⁴) or the limited use at a higher pressure (acetylene, butane⁵). The important criterion for the selection of the filling gas is also the contents of the hydrogen atoms in the molecule which should be as high as possible⁶ because of measuring the lowest tritium concentrations.

According to these criteria ethane was found to be the most convenient hydrocarbon which was prepared by hydrogenation of acetylene; hydrogen was prepared by reduction of tritium oxide. The whole procedure consisted of the withdrawal of the air humidity and of the preparation of hydrogen and ethane.

EXPERIMENTAL

Chemicals and Materials

The materials used were acetylene (technical grade), argon (ČSN 6543), palladium on asbestos, molecular sieve Calsit 5A and Nalsit 13X (Slovnaft, Bratislava), porous polymer marketed under the name Porapak Q 100—120 mesh (Waters Associates, Framingham, Mass., USA), pure magnesium powder, nickel catalyst 40—01 (Chemické Závody SČSP, Záluží v Krušných horách), spring water (Szeczeny, Hungary), silver wool.

Withdrawal of the Air Humidity

The withdrawal of the air humidity was carried out by adsorption on the molecular sieve Calsit 5A within the temperature range 5—30°C at the air flow rate of 60 l/min. In the run of the desorption the adsorption tubes containing the molecular sieve were inserted into the furnace 5

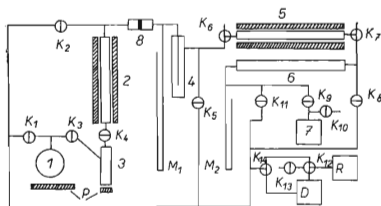


FIG. 2

Diagram of Apparatus for the Preparation of Hydrogen

1 Evaporation flask, 2 reduction furnace, 3 boiling flask, 4 trap, 5 purification furnace, 6 absorption tube, 7 vessel with hydrogen, 8 separator, R rotatory pump, D diffusion pump, P furnace, M manometer, K_1 — K_{14} vacuum stopcocks.

(Fig. 1) which was evacuated prior to heating up to 350°C. Water desorbed at this temperature was swept out by the pure argon of the flow rate of 20 ml/min and collected in the traps 6 and 7 at -78°C. The procedure was completed after 6–8 hours.

Preparation and Purification of Hydrogen

First of all the sample of water obtained from the desorption apparatus was filtrated and transferred to the flask 1 of the dehydrogenation apparatus, shown in Fig. 2. The stainless steel tube filled with the weighed amount of dried magnesium was inserted into the furnace 2 and the furnace 5 was switched on. After the temperature increased up to the operating range (580 and 200°C for the furnaces 2 and 3 respectively) the vacuum was closed by the stopcocks K_2 , K_5 , K_8 and K_{11} and stopcock K_4 was opened. By switching on the furnace *P* the sample of water was gradually evaporated with subsequent reduction by passing through the heated magnesium bed. Hydrogen prepared in this way was separated from the magnesium particles and eventual water if necessary in the traps 8 and 4 respectively. Then, purified hydrogen was dried quantitatively and stored in the bulb or immediately used for the preparation of ethane.

Preparation and Purification of Ethane

Acetylene and hydrogen were purified before use. The vessels containing C_2H_2 and H_2 were connected with the inlets *D* of the apparatus shown in Fig. 3. The hydrogenation catalyst 4001 was placed into the furnace 1 and evacuated to 10^{-3} Torr before heating was started. After a sufficient amount of the hydrogenation mixture was passed through the furnace 1 (Fig. 3) the resulting mixture was transferred to the traps V_3 (at -82°C) and V_4 (at -196°C) where ethane

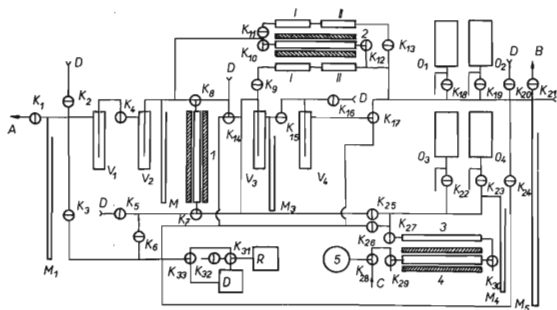


FIG. 3

Diagram of Apparatus for the Preparation and the Purification of Ethane

1 Hydrogenation furnace, 2 purification furnace, 3 absorption tube, 4 purification furnace, 5 hydrogen reservoir, A inlet of acetylene, B outlet to gas chromatograph, C inlet of hydrogen, D outlets for the sample withdrawal, O_1 – O_4 bulbs, V_1 – V_4 traps, M_1 – M_5 manometers, *I* and *II* absorption tubes, *R* rotatory pump, *D* diffusion pump, K_1 – K_{33} vacuum stopcocks.

produced was quantitatively collected and the excess of hydrogen was removed. Then, the stopcocks K_8 and K_7 were closed and the system was evacuated to 10^{-3} Torr. The purification of ethane itself was carried out by repeated vacuum condensation and expansion from the V_4 to the V_1 through the V_2 and V_3 (at -78°C) wherein it was passed through the tubes I, II and the furnace 2. This cycle was repeated 5—8 times (Fig. 4). Finally, ethane prepared and purified in such a manner was collected in the V_4 and transferred either to the special vacuum flask through the stopcocks K_{16} whereby the K_{15} was closed or through the K_{17} , K_{18} and K_{19} into the bulbs O_1 and O_2 respectively. By means of the stopcock K_{21} it was possible to fill directly the sampling system of the gas chromatograph.

If some other hydrogen was used instead of that prepared as described above, first the bulb 5 was fed and hydrogen was passed through the furnace 4 (palladium on asbestos at 450°C) and drying tube. Hydrogen purified in this way was either stored in the bulbs O_1 and O_2 or passed through the stopcocks K_{26} and K_{27} to be instantaneously used in the hydrogenation.

Analytical Methods

The whole kinetics of the hydrogenation reaction of ethylene as well as the purification procedure of ethane was followed by a gas chromatograph. The apparatus used was of our own design equipped with a double thermal conductivity cell (the bridge current of 120 mA) of the Research Institute of Organic Syntheses, Rybitví, and a recorder of 0—0.1 mV full scale sensitivity (Kipp Co., model BD5). Hydrogen was used as the carrier gas at the pressure of 460 Torr. The column was packed with Porapak Q, Nalsit 13X or with 15% w/w of β, β' -oxydipropionitrile on 0.16/0.2 mm Chromatone N—AW.

Measurement of Activities

After the conversion to ethane the concentration of tritium was measured by a proportional counter combined with a shielding counter. The total sensitive volumes of the inner counter and that of the shielding counter were 0.5 and 0.82 l respectively. During the course of the measurement the detector was placed into the lead shielding of the thickness of 10 cm.

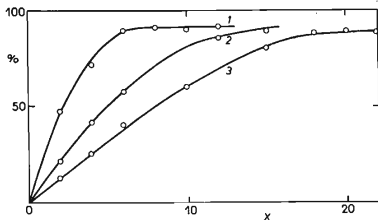


FIG. 4

Dependences of the Ethane Conversion (%) upon the Number of the Hydrogenation Cycles

1 Flow rate 2 l/min, 2 8 l/min, 3 16 l/min, at the constant temperature of 150°C and the ratio of the parent compounds $\text{C}_2\text{H}_2/\text{H}_2 = 1/2.5$.

DISCUSSION AND RESULTS

The hydrogenation reaction of acetylene is very strongly dependent on the operating temperature, on the ratio of the individual components of the reaction mixture and on the flow rate. For this reason our attention was mainly focussed to the investigation of the optimum conditions of the reaction in question. Under the given conditions the reaction yield of 92–96% of ethane is obtained. The samples of ethane supplied by Slovnaft, Bratislava served as an analytical standard. The operating characteristic of the proportional counter (as described earlier⁷) filled by ethane prepared and purified in such a procedure as described above has the plateau of the length of almost 600 V.

The method of determining the extremely low tritium activities by means of the gas filled counters is most frequently used because of the high sensitivity for the low energetic radiation and high efficiency of the detection. In our case the natural activity of tritium in the troposphere the value of which varies around 300 TU (1 TU = 3.2 pCi : 1 H₂O) is considered as a low activity at present. Such activities of tritium in water are measured with the maximum error of 5%. The actual concentration value has 99% of probability in this range. The liquid scintillation can be a competitive method mainly for the measurement of the ³H concentrations higher than 500 TU. Other methods of determining low tritium activities, e.g. the application of the cloud or bubble chambers did not make themselves useful.

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