Synthesis and Purification of Propyne-3-^{14}C

In the course of our gas phase radiolysis studies [1] need arose to have carbon-14 labelled propyne available. The material was to be specifically labelled in the methyl group and the required specific activity was 1 mc/mmole. Rather than employing the well established but time consuming method of reacting sodium acetylide with an alkyl halide in liquid amonia [2] we used one of the recently prepared alkali acetylide addition compounds which are stable at room temperature and which can be stored without elaborate precautions [3]. We proceeded as follows :

Inside a glove box with dry nitrogen atmosphere .2 grams of lithium acetylide, complexed with 1,2-ethanediamine *, was placed into an Erlenmeyer

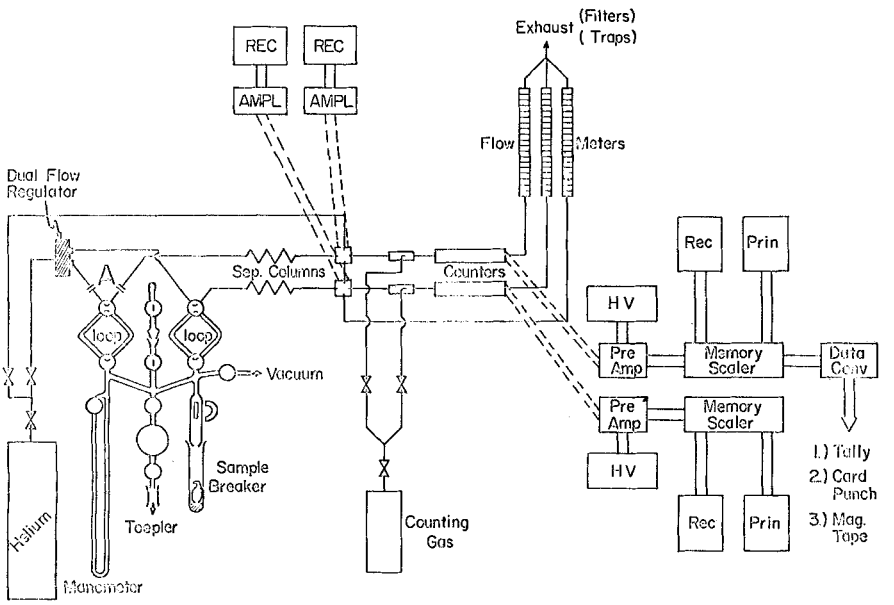

FIG. 1. Dual line radio gaschromatograph designed for all investigations involving sealed samples or aliquots transferred from a vacuum line. The radioactivity data output is largely automized.

* Purchased from Foot Mineral Co., Exton, Pennsylvania, U.S.A. (Lot No. 403-2).

flask fitted with a ground glass joint. A teflon coated stirring bar was added, a stopcock with a matching joint inserted and the reaction flask attached to a vacuum line.

After pumping the nitrogen from the reaction vessel, .5 mc methyl iodide-^{14}C * was frozen from the shipping container into it. At room temperature the reaction was allowed to procede for 6 hours while the stirrer was kept in vigorous motion. Then the gaseous reaction products were frozen into a storage vessel on the vacuum line.

Figure 1 shows one of the radio gaschromatographs used in our laboratory for a large variety of studies. The counting procedures with digital and analog output have been described elsewhere [4].

A transfer bulb, containing a small portion of the reaction product, is attached between the two injection loops as seen in Figure 1. Aliquots can then be transferred into the loops by toeplering.

The analyses and the purification were performed with a Safrole column (1/4 inch stainless steel, 40/60 mesh Firebrick, 35 feet, 0° C). The radio activity was monitored with a 46 ml internal proportional quartz counter** which has a detection efficiency of >98% for carbon-14. Propane served as counting gas, giving plateau lengths of about 1,000 volts. As shown in Figure 1, the counting gas is added after the fractions pass the thermal conductivity cell [5].

The analysis of the gaseous reaction product revealed several ^{14}C containing compounds as well as a large amount of non-radioactive acetylene (Table 1). We therefore transferred all the material from the storage

TABLE 1. Summation of the results obtained. The specific activities of the products indicate that the purchased methyl iodide had a higher specific activity than stated by the vendor. The propyne yield is approximately 20%, based on the amount of methyl iodide used.

Compound	Reaction mixture mass rel. to propyne = 100	Reaction mixture spec. activity mc/mmole	Purified comp. spec. activity mc/mmole
$CH_4 + CO$	Unknown	0	
$C_2H_6 + C_2H_4$	.294	$1 \pm .25$	
CO_2	2.4	0	
C_2H_2	510	0	
C_3H_4 (allene)	.11	$1 \pm .4$	$1.2 \pm .05$
C_3H_4 (propyne)	100	$1 \pm .2$	$1.2 \pm .02$

* Purchased from New England Nuclear Co., Boston, Mass., 02118, U.S.A. (specific activity 1 mc/mmole).

** Purchased from Roman Scientific Glassware, 57 Everett St., Patchogue, Long Island, New York, U.S.A.

vessel into an injection loop and attached it in position A indicated in Figure 1. Monitoring the separation by thermal conductivity measurement allows the precise timing for freeze trapping of the fractions. The purified propyne was transferred back to the storage vessel. A subsequent radio-purity check showed $>99.999\,\%$ propyne-3-^{14}C.

One of the carbon-14 containing products was identified as allene (C_3H_4) on the basis of its retention volume. It cannot be excluded, however, that this peak represents cyclopropene or both compounds. For either molecule, specific labelling can be assumed (allene in C_1, cyclopropene in the methylene position).

The results are summarized in Table 1.

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