PREPARATION, PURIFICATION, ANALYSIS AND STORAGE OF MULTITRITIATED PROPANE

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Received May 22, 1978

SUMMARY

Multicurie amounts of propane-T_x have been obobtained with typical yields of ca. 30% from the reaction of C_3H_8 with excess T_2 over a Ni catalyst. The mass spectrometric analysis of the reaction product purified by preparative glc gave the following distribution: C_3H_8 16 mol%, C_3H_7T 13 mol%, $C_3H_6T_2$ 25 mol%, $C_3H_5T_3$ 29 mol%, $C_3H_4T_4$ 12 mol%, propanes containing more than 4 T atoms 5 mol%. The ^3H nmr spectra of the sample showed that the ratio of tritium atoms contained in the methyl groups to those contained in the methylene group is 2.4 ± 0.3.

INTRODUCTION

Multitritiated hydrocarbons, containing at least two radioactive atoms in the same molecule, are used as precursors of labelled carbonium ions to study ion-molecule reactions in gaseous systems at atmospheric pressure, or in condensed systems (1-6).

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0362-4803/78/0015-0703$01.00

The present paper describes the preparation of multitritiated propane, containing several radioactive atoms in the same molecule, based on the isotopic exchange between C_3H_8 and an excess of T_2 over a Ni catalyst. In order to establish the most sutiable experimental conditions, the exchange has been previously investigated using deuterium gas (7) and analyzing the products by mass spectrometry.

EXPERIMENTAL

Materials

Research grade propane from Deutsche L'Air Liquid, having a stated purity of 99.154 mol%, was used without further purification. Tritium gas was obtained from the Radiochemical Centre Amersham, England, with a stated purity of 98 mol%, the major impurity being ^3He. The reduced and stabilized Ni catalyst was obtained from Alfa Products.

PROCEDURE

Preparation

For the preparation of propane-D_x the catalyst is introduced into the pyrex apparatus illustrated in Figure 1A, which is then connected to a vacuum line, outgassed at 420 ^oC for three hours, then filled with D_2 (ca. 500 Torr) and heated at 110 ^oC for one hour. After this operation, intended to eliminate most of the hydrogen contained in the system (catalyst + vessel), the D_2 gas is discarded, then a C_3H_8 + D_2 mixture is introduced into the apparatus to a total pressure of 750 Torr. After freezing C_3H_8, the ampoule is sealed off at c,

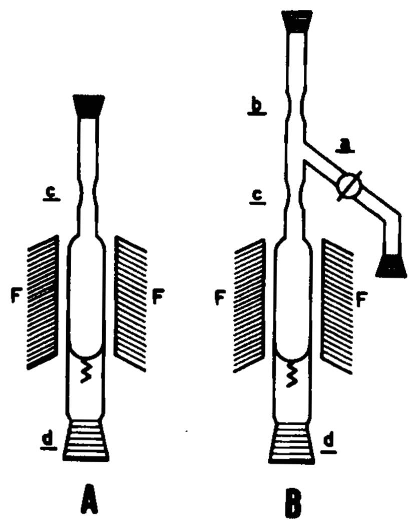

Fig. 1. A. Apparatus for the preparation of propane-D_x.
B. Apparatus for the preparation of propane-T_x.

then heated to 110 °C for one hour. After the exchange has occurred, a vaccum stopcock is attached at d, the apparatus attached to a vacuum line and thoroughly outgassed. The gaseous mixture is withdrawn from the ampoule by breaking the seal, and analyzed by mass spectrometry using a Hewlett Packard Model 5982 A instrument, equipped with a dual electron impact/chemical ionization source.

The apparatus for the preparation of propane-T_x is shown in Fig. 1B. After activation of the Ni catalyst (500 mg), the apparatus is sealed off at b, T_2 (ca. 7 Ci) is introduced via stopcock a, and the system is heated to 110 °C for one hour, in order to remove any labile H present in the catalyst or on the walls. The tritium gas is then withdrawn with a Toepler pump, and new T_2 is added, together with C_3H_8, via stopcock a.

Propane is frozen with liquid nitrogen, the apparatus is sealed off at c, and heated for one hour at 110°. The apparatus is then connected to a vacuum line via tubing d, cooled with liquid nitrogen, the break seal broken and the excess T_2 pumped off and recovered.

Analysis

The crude tritiated propane (ca. 0.35 ml) is transferred into a 125 ml pyrex bulb, except for a small fraction used for analytical purposes. The radio gas chromatographic analysis has been carried out with a Hewlett Packard Model 7620 A, equipped with a 6 m long, 3.5 mm i.d. column, packed with 50/80 mesh Porapak A, operated at 70 ^{o}C for 30 min and then with a temperature gradient of 10 ^{o}C/min until 190^{o}. He-carrier gas was used at a flow rate of 50 ml/min.

The outlet of the column was connected to a 10 ml flow proportional counter from Berthold-Frieseke, operated at a total flow rate of 100 ml/min, after diluting the gas chromatographic effluents with CH_4 (50 ml/min). The results of radio gas chromatographic analysis are given in Table I, indicating a 31.2% radiochemical yield of propane-T_x.

The isotopic analysis of the products was carried out with a AEI M7 702 mass spectrometer, analyzing the mass region between the m/e values 36 and 60, and correcting for the background, determined by analyzing under the same conditions a C_3H_8 sample. The results are given in Table II. It should be pointed out that the total T content of the reaction product, as determined by mass spectrometry, leads to a specific activity value which is in excellent agreement with those determined by radiometric measurements.

Table I. Radiochemical yields of tritiated products from the C_3H_8/T_2 exchange.

Products	Activity mCi	Relative yields of Products (%)	Yield relative to total T_2 employed (%)	% of theoretical yield
HT	8,1	0,597	0,112	0,203
T-methane	69,2	5,07	0,953	1,730
T-ethylene	1,3	0,097	0,018	0,033
T-ethane	29,2	2,15	0,402	0,730
T-propylene	0,9	0,073	0,012	0,023
T-propane	1249,0	91,6	17,204	31,225
X_1	0,1	0,008	0,001	0,003
X_2	1,5	0,113	0,021	0,038
X_3	1,5	0,113	0,021	0,038
X_4	1,1	0,081	0,015	0,028
X_5	1,1	0,081	0,015	0,028
X_6	1,4	0.105	0,019	0,035
Σ	1364,4	100	18,793	34,114

Table II. Mass spectrometric analysis of tritiated propanes.

Compounds	m/e	%	mCi
C_3H_8	44	16,06	-
C_3H_7T	46	12,78	75,89
$C_3H_6T_2$	48	24,82	295,18
$C_3H_5T_3$	50	28,59	510,57
$C_3H_4T_4$	52	11,90	283,46
$C_3H_3T_5$	54	3,34	99,32
$C_3H_2T_6$	56	2,11	75,33
C_3HT_7	58	0,10	4,20
C_3T_8	60	0,29	14,01
Σ		99,99	1357,96

DISCUSSION

Table III gives the percentage of $C_3H_xD_y$ propanes from the C_3H_8/D_2 isotope exchange reactions carried out under different conditions. These data have been used to evaluate the most suitable experimental conditions, including the nature and amount of the catalyst, the relative concentration of propane and D_2, and the reaction time. From Table III it is apparent that Ni supported on

Table III. Effect of experimental conditions on the C_3H_8/D_2 exchange[a].

Temperature °C	Catalyst	mg	Vessel volume (ml)	C_3H_8 pressure (Torr)	D_2 pressure Torr	Relative abundances of C_3H_8 mass peaks (%) m/e 44	45	46	47	48	49	50	51	52
110	Pd 10% on carbon	70	2,0	20	700	93,03	4,33	2,25	1,04	0,35	-	-	-	-
110	"	150	2,0	20	700	77,54	12,28	6,99	2,46	0,73	-	-	-	-
110	"	150	2,0	60	680	82,75	9,38	5,60	1,85	0,41	-	-	-	-
110	Ni on Kieselghur	150	2,0	30	700	20,57	11,28	12,17	14,79	15,37	12,52	7,90	3,83	1,56
250	"	150	2,0	30	700	(b)								
110	"	150	2,0	80	670	25,79	28,48	24,25	13,89	5,26	1,74	0,60	-	-
110	"	86	2,0	50	700	52,93	9,35	6,63	6,41	6,85	5,76	5,98	3,70	2,39
110	"	400	6,0	50	700	22,4	11,1	10,0	11,0	12,7	13,0	10,9	6,8	2,4
110	"	600	6,0	50	700	22,52	12,92	11,14	10,93	13,21	12,64	9,89	4,68	2,11
110	"	600	6,0	80	670	47,40	8,52	8,21	8,32	9,46	6,86	5,82	3,85	1,56
110	"	800	6,0	80	670	48,78	7,46	6,19	5,24	6,95	8,29	8,22	5,80	3,06

(a) Mean value of several experiments.

(b) Extensive C_3H_8 hydrogenolysis

kieselgur gives higher conversions than Pt supported on carbon, and that the yields of propanes-D, while insensitive to the vessel volume, are strongly affected by the amount of catalyst. Finally the yields are strongly affected by the D_2/C_3D_8 ratio, decreasing when the ratio drops below 10:1. The most suitable temperature is ca. 110 ^oC, since the reaction becomes slow at lower temperatures, wile extensive fragmentation of propane takes place at higher temperatures.

A comparison of the results in Table I and II shows that the amount of the unreacted propane is considerably lower in the exchange with T_2 (16% vs. 22% in the exchange with D_2). Furthermore, most of the activity is found in the $C_3H_6T_2$ (24.8%) and $C_3H_5T_3$ (28.6%) species, with appreciably lower percentages for the other isotopic species, which contrasts with the more uniform distribution observed in the D_2 exchange.

Finally, C_3T_8 is formed with much lower yield than C_3D_8. Undoubtedly, some of the differences must arise from the self-radiolysis of the tritiated products, the specific activity of which corresponds to about $8 \cdot 10^4$ Ci per mole.

Such specific activity levels pose several problems on the purification and especially the storage of propane-T_x.

Purification and storage

The crude reaction product was diluted with C_3H_8 (2 mmoles), then purified by preparative glc using the apparatus shown in Fig. 2.

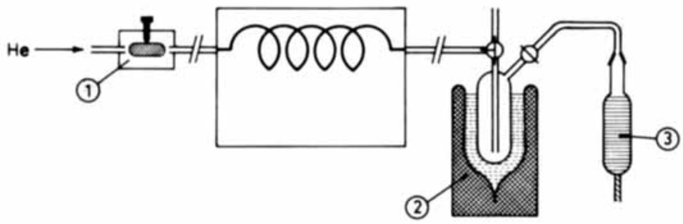

Fig. 2. Apparatus for the gas chromatographic purification of tritiated propane: (1) Ampoule breaker for injection; (2) Liquid nitrogen trap; (3) Molecular sieve trap.

A fragile ampoule, containing the crude sample, was broken in the stream of the He-carrier gas and injected into the same column used for the gas chromatographic analysis. The central cut of the propane peak was collected in a trap cooled with liquid nitrogen, and its purity determined by radio glc. The results, shown in Table IV, indicate that the radiochemical purity of the purified sample is 99.7%, the major impurity being propylene-T (ca. 0.15%). The purified samples were stored, following dilution with a large excess of inactive propane, and addition of a small amount of NH_3, as an ion interceptor, and of O_2 as a radical scavenger.

Distribution of T: the methyl/methylene ratio

Since the use of propane-T_x as a source of decay ions required the knowledge of the T distribution among non-equivalent molecular positons, a 15 mCi sample dissolved in C_6D_6 was analyzed by ^3H nmr in a Jel 100 MHz spectrometer. Accumulation of 34.000 scans allowed to obtain nmr spectra showing two typical multiplets, assigned to

Table IV. Radiochemical purity of propane after preparative glc.

Compounds	Activity mCi	%
HT	$3,1\cdot10^{-2}$	$3,1\cdot10^{-3}$
Methane-T	$4,4\cdot10^{-2}$	$4,3\cdot10^{-3}$
Ethylene-T	$3,3\cdot10^{-2}$	$3,3\cdot10^{-3}$
Ethane-T	0,19	$1,9\ 10^{-2}$
Propylene-T	1,52	$1,5\ 10^{-1}$
Propane-T	1011	99,70
$X_1^{(a)}$	0,14	$1,4\cdot10^{-2}$
$X_2^{(a)}$	1,11	$1,1\cdot10^{-2}$
Σ	1014,1	99,905

(a) Unidentified C_4 hydrocarbons

methylene-T and methyl-T atoms, respectively. Owing to the relatively low activity of the sample, the percent abundance of the individual partially tritiated propanes could not be determined with any degree of confidence. However, integration of the corresponding multiplets allowed determination of the ratio of the tritium atoms contained in the methyl groups vs. those contained in the methylene group. The value observed, 2.4 ± 0.3, is lower than the expected one for random labelling (3.0), and suggests preferential tritiation at the methylene positions.

ACKNOWLEDGEMENT

The authors wish to acknowledge the continued interest of Prof. F. Cacace in their work, and M. Attinà for the mass spectrometric analysis of propane-D_x. R.C. acknowledges financial support from the Italian Government.

The authors wish to thank R. Ehrenkaufer for Tritium NMR Spectrometry obtained at the 'Facility for Biomedical NMR on Radioactive Samples' (at the State University of New York at Stony Brook, USA) which is supported by the National Institutes of Health, Division of Research Resources grant No. RR01039.

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