

Note

Radio-gas chromatography of tritiated compounds*

JIUNN-GUANG LO* and JONG-CHEN NIEH

Institute of Nuclear Science, National Tsing Hua University, Hsinchu 300 (Taiwan)

(Received December 5th, 1984)

In previous work we used a flow system surrounding an NaI(Tl) scintillation detector for the measurement of trace amounts of chromium and the iodine isotope exchange reaction^{1,2}, with high sensitivity and good reproducibility. Both studies used ⁵¹Cr and ¹³¹I β -emitters as radioactive tracers. The low-energy tritium nuclide β -emitter was used as a radiotracer throughout. The radioactivity of gaseous tritiated compounds is measured better with an internal flow-proportional counter^{3,4} than with other detection methods. Using the former detector system the kinetic reactions of tritium or halogens with hydrocarbons were studied⁵⁻⁷.

A refined method has now been established for the separation and determination of tritiated compounds by radio-gas chromatography, and the system has been used in a kinetic study of the recoil tritium reaction with ethanol in the gas phase. The main products found in the mass of radio-chromatograms were labelled hydrogen, methane and ethanol whereas other minor products were found only in the radio-chromatogram. Helium, hydrogeniodide and iodine were added to the system to serve as moderators or scavengers in order to establish the reaction mechanisms.

EXPERIMENTAL

Radio-gas chromatography

A Shimadzu (Tokyo, Japan) Model GC-9A gas chromatograph, was used. Fig. 1 shows the radio-gas chromatographic system. From this system two chromatograms were obtained using two different detectors, one of mass concentration with a thermal conductivity detector and the other of radioactivity of tritium with an internal flow-proportional counter. The counting data and radio-chromatograms were stored, analysed and plotted in an MCA/Apple II data acquisition analysis system.

A 6 ft. \times 1/8 in. Porapak Q column was used with helium as the carrier gas. The column temperature was increased from 0 to 150°C at 1°C/min. The thermal conductivity detector was kept at a constant temperature of 120°C. *n*-Propane as the counting gas was mixed with the eluate from the chromatographic column before entering the flow proportional counter, in which brass was used as the cathode and a central 25- μ m tungsten wire as the anode, the temperature being kept at 100°C to prevent alcoholic compounds being deposited in the counter. The slope of the plateau

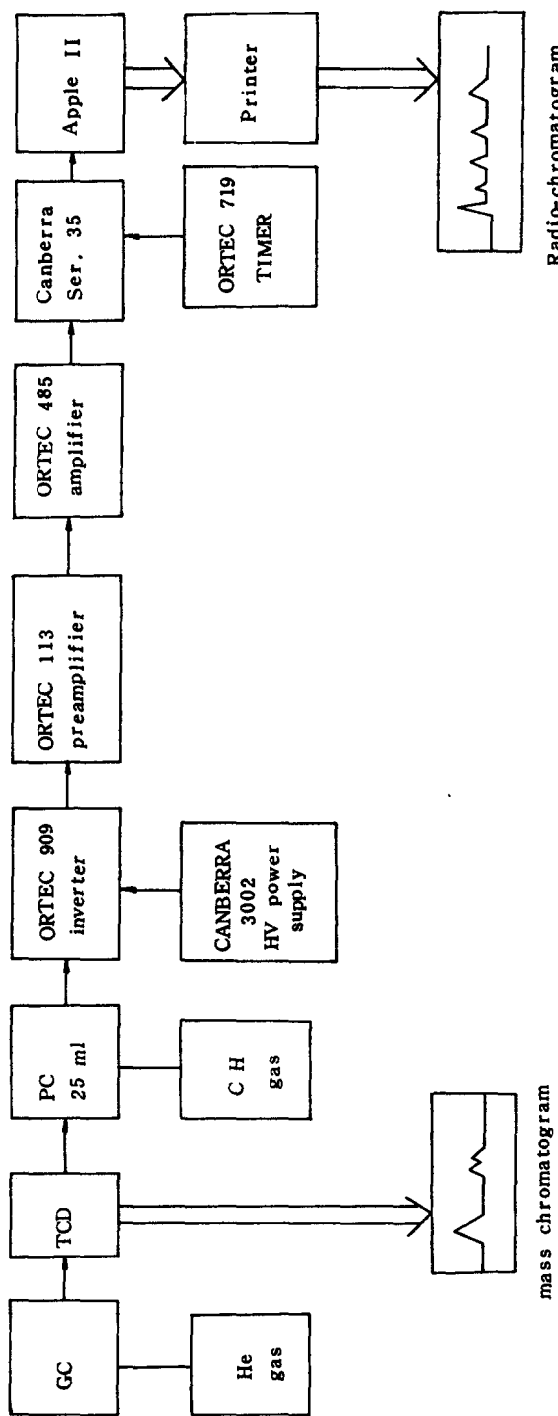


Fig. 1. Schematic diagram of system for radio-gas chromatography. PC = Proportional counter; TCD = thermal conductivity detector; GC = gas chromatograph.

is less than 5% per 100 V. The ratio of propane to helium pressure was 2:1. Counting data previously accumulated in a Canberra 35 MCA system were transferred to an Apple II microcomputer. The peak area in the radio-chromatogram was integrated by a computer program⁸ consisting of smoothing, peak search, integral peak area and expand modes for small peaks. The radio-chromatogram was plotted by a CP-80 printer (C.T.I, Tokyo, Japan).

Sample preparation for neutron irradiation

Sample preparation for neutron irradiation was carried out in a vacuum system. The vapour pressure of ethanol in the quartz ampoule was 30–120 Torr and the ethanol was mixed with ^3He as a tritium source. Under neutron bombardment, the high-energy tritium recoiled from the nuclear reaction of $^3\text{He}(n,p)\text{T}$ and reacted with ethanol instantaneously in the ampoule. Different amounts of He, HI, O_2 and I_2 were added in the system to serve as moderators and scavengers. The neutron irradiation was performed at the 1 MW Tsing Hua open-pool reactor for 10 min, using a pneumatic tube. The thermal neutron flux was $2 \times 10^{12} \text{ n cm}^{-2} \text{ sec}^{-1}$.

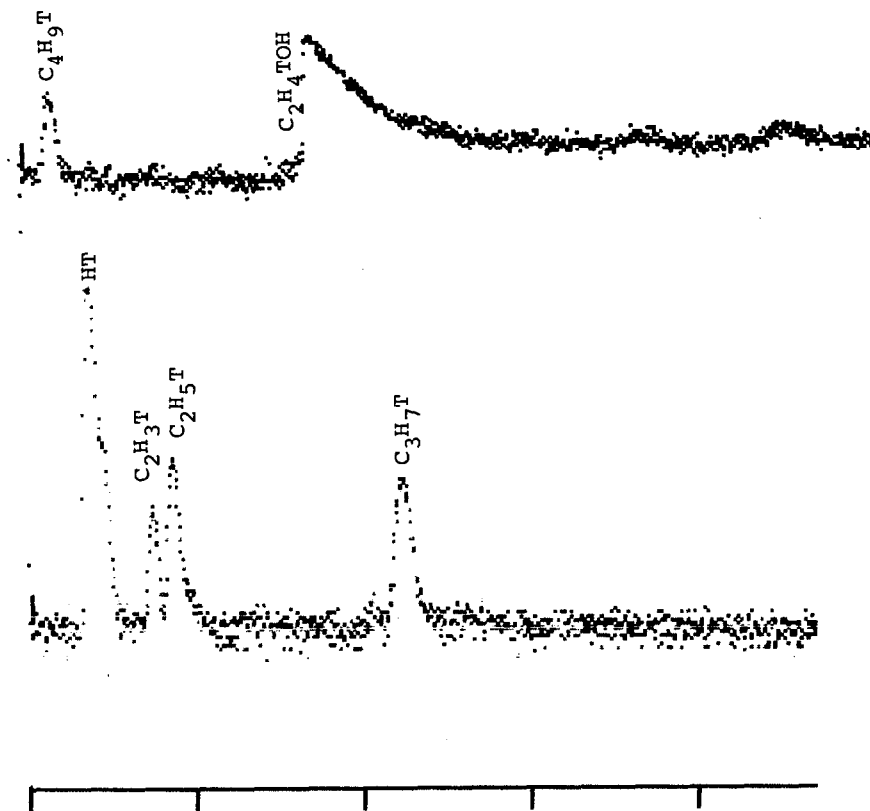


Fig. 2. Radiochromatogram of tritiated compounds. Conditions: 1, 20 Torr He and 60 Torr $\text{C}_2\text{H}_5\text{OH}$; 2, internal flow proportional counter at 100°C .

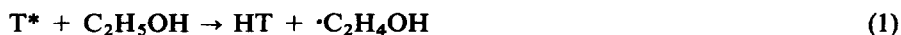
RESULTS AND DISCUSSION

Radio-gas chromatogram

Several products are produced by hot atom chemical reactions during the neutron irradiation. The main products are labelled hydrogen, methane and ethanol, and these products are found in both the mass and radio-chromatograms. Low mass concentrations of minor tritiated products compounds such as aldehydes, methanol, propane and butane are found only in the radio-chromatogram, as illustrated in Fig. 2. In general, a 3-ft. Porapak Q chromatographic column gives suitable retention times for mass separation. However, for the products in the eluate being detected in the large volume of the flow-proportional counter (25 ml), the radioactive peaks are broader than mass peaks, whereas the 6-ft. column is used to avoid overlapping peaks in the radiochromatogram.

Kinetic study of recoil tritium atoms with ethanol

Recoil tritium atoms react with ethanol in the presence of HT scavenger to form mainly labelled ethanol, ethane and HT, which are produced by the hot atom chemical reactions. The yields of the various products are given in Table I. The HT, CH₃T and C₂H₅T are products of the following hot abstraction reactions:



Labelled ethanol is formed in the following hot substitution reaction:



The yields of the saturated hydrocarbons C₃H₇T and C₄H₉T are virtually zero in the presence of both scavengers, presumably owing to thermal chain reactions.

TABLE I

YIELDS OF TRITIATED COMPOUNDS (%) IN THE SCAVENGER SYSTEM

Product	Molar fraction of He (%)				I ₂ (2 mg)
	0	30	20	10	
HT	55	49	50.2	52	} 45.5
CH ₃ T	4.1	8.6	8.8	7	
C ₂ H ₃ T	0.8	4	3.3	2.2	0.5
C ₂ H ₅ T	2.9	3.2	3.1	3.1	1.8
C ₃ H ₇ T	2	N.D.*	N.D.	0.12	N.D.
CH ₂ TOH	0.15	0.18	0.2	0.21	0.1
CH ₃ COT	0.3	0.35	0.32	0.31	0.2
n-Butane	0.6	N.D.	N.D.	N.D.	N.D.
C ₂ H ₅ OH(T)	33.8	33.9	33.5	3.4	48.9

* N.D. = not detected.

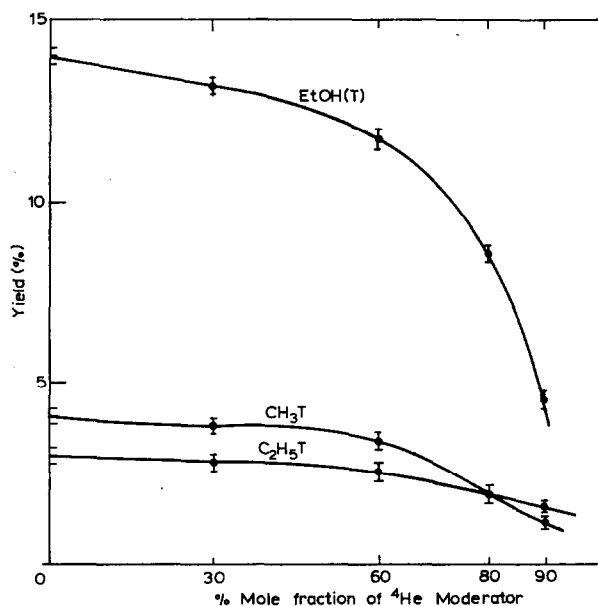


Fig. 3. Moderator effect of hot species.

Helium is added to the system to serve as a moderator of hot species. The yields of CH_3T , $\text{C}_2\text{H}_5\text{T}$ and $\text{C}_2\text{H}_5\text{OH(T)}$ versus the amount of moderator are plotted in Fig. 3. The yields of these products decreased when the pressure of helium was increased, as indicated in Table II. From the moderator effect it can be concluded that these products are formed by hot chemical reactions. The HT yield is even higher in the presence of a scavenger, which gives a higher G value of HT in the gas-phase radiolysis of ethanol⁹. Similar results are obtained for the major products ethanol, CH_3T and HT in the liquid phase⁹⁻¹¹ (see Table II), except for the yields of propane and butane owing to the high radical thermal reaction in the gas phase.

TABLE II

YIELDS OF TRITIATED COMPOUNDS (%) IN THE MODERATOR SYSTEM

All samples contained 30 Torr of ³He and 60 Torr of ethanol.

Product	Molar fraction of ⁴ He (%)			
	0	80	60	30
HT	55	58	55.5	55
CH ₃ T	4.1	2	3.6	4
C ₂ H ₃ T	0.8	2	1.4	0.9
C ₂ H ₄ T	2.9	2	2.2	2.6
C ₃ H ₇ T	2	3.5	2.8	2.4
CH ₂ TOH	0.15	0.41	0.31	0.27
CH ₃ COT	0.3	0.26	0.28	0.32
<i>n</i> -Butane	0.6	3	1.2	1
C ₂ H ₅ OH(T)	33.8	28.6	31.8	33.5

TABLE III

YIELDS OF TRITIATED PRODUCTS (%) FROM REACTIONS OF RECOIL TRITIUM ATOMS WITH ETHANOL

Labelled compound	Ref. 9, irradiation at 20°C for 2 h, vacuum	Ref. 10, irradiation at 150°C for 5 h air	This work liquid phase	
			At -78°C for 15 min, air	At 20°C for 10 min, vacuum
HT	50.20	60.1	62.1	55
CH ₃ T	3.45			4.1
C ₂ H ₅ T	} 1.67	0.4	0.7	2.9
C ₂ H ₃ T			0.1	0.8
C ₃ H ₇ T	} 0.39	0.3	—	2
C ₄ H ₉ T			—	0.6
CH ₂ TCHO	1.97	1.8	0.8	0.3
CH ₂ TOH	0.98	} 33.4	0.8	0.15
C ₂ H ₄ TOH	41.34		35.5	33.8

ACKNOWLEDGEMENT

This work was supported by the National Science Council of Taiwan.

REFERENCES

- 1 J. G. Lo and S. J. Yeh, *J. Chromatogr. Sci.*, 18 (1980) 359.
- 2 J. G. Lo, M. C. Lee and S. J. Yeh, *J. Chromatogr. Sci.*, 20 (1982) 353.
- 3 R. Wolfgang and C. F. Macky, *Nucleonics*, 16 (1958) 69.
- 4 J. K. Lee, E. R. C. Lee, B. Musgrave, Y. N. Tang, J. W. Root and F. S. Rowland, *Anal. Chem.*, 34 (1962) 741.
- 5 L. D. Spicer and A. A. Gordus, *Chem. Eff. of Nucl. Transform., Proc. Symp. 1964*, 1 (1965) 185.
- 6 D. S. Urch, *Inorg. Chem. Ser. One*, 1972, 8 (1972) 113.
- 7 D. S. Urch, *Inorg. Chem. Ser. Two, 1974-1975*, 8 (1975) 46.
- 8 P. J. Manly, *Transfer Program Operation and Reference Manual*, Gamma Corp., Los Angeles, CA, 1983.
- 9 J. Hoff Wilford, Jr. and F. S. Rowland, *J. Amer. Chem. Soc.*, 79 (1956) 4867.
- 10 A. N. Nesmeyanov, T. W. Chang and E. S. Filatov, *Radiokhimiya*, 5 (1963) 515.
- 11 J. G. Lo and S. M. Yang, *Proc. Nat. Sci. Council. Repub. China*, 8 (1984) 171.