Wall Effects in Gas-Phase Recoil Tritium Chemistry

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THE chemistry of recoil tritium atoms with simple hydrocarbons (RH) has been extensively studied.[1] Up to now it has been assumed that all the labelled molecules, produced in the presence of a radical scavenger, resulted from homogeneous gas-phase reactions and that the way in which the ratio HT : RT changes with added inert gas moderator may be used to test theories of 'hot' reactions.[2] However, when recoil tritium [^{3}He $(n, p)^3$H] reacts with ethane, either at low pressures or in sample tubes packed with quartz wool, a large increase in the relative amount of HT is observed (Table 1),

TABLE 1

Type of sample tube	Quartz tube (Vol. 16 c.c.)			Tubes packed with quartz wool		
Pressure of C_2H_6	73	13·9	4·1	76	4·8	27·5
Pressure of ^{3}He	1	1·5	2·0	4·75	5·0	4·7
Pressure of O_2	3	1·6	0·3	4·0	4·25	35
HT	178	213	405	460	740	425
CH_3T	11·0	10·8	11·7	10·3	9·1	9·5
C_2H_5T	100	100	100	100	100	100
C_2H_3T	7·8	7·0	7·5	5·4	5·2	4·5

All pressures are in cm. Hg. All yields are relative to $C_2H_5T = 100$.

[1] Reviews by I. G. Campbell, *Adv. Inorg. and Radiochem.*, 1963, **5**, 135; F. Schmidt-Bleek and F. S. Rowland, *Angew. Chem.* (*Internat. Edn.*), 1964, **3**, 769. R. Wolfgang, U.S. Atomic Energy Commission Report NYO-1957-50; Also to appear in *Progr. in Reaction Kinetics*, **3**.

[2] P. J. Estrup and R. Wolfgang, *J. Amer. Chem. Soc.*, 1960, **82**, 2665. R. Wolfgang, *J. Chem. Phys.*, 1963, **39**, 2983.

suggestive of a wall effect. In these sample tubes, as in those containing excess of moderator,[3,4] the path length of the recoil triton will be such that a greater percentage of the tritons will collide with a quartz surface than in a tube filled with a higher pressure of ethane. The sample that contains over 50% oxygen shows that this increase in HT is not due to thermal tritium atoms diffusing off the wall[4] (cf. ref. 4, p. 36) and then reacting with hydrocarbons; if this were so the relative HT yield in this tube would have returned to 180, the normal value.

To find the source of this excess of HT we irradiated tubes containing pure C_2D_6 (Merck, Sharpe, and Dohme of Canada, 98%), oxygen, and helium-3 at low pressures and at high moderator concentrations. Using an eight-foot activated alumina column (−196° c) to separate HT and DT,[5] we found that a large percentage of the tritiated hydrogen was in fact HT and not DT (Table 2). The quartz used was ordinary grade Vitrosil (Jencons Ltd.)[2]; the tubes were flamed out under vacuum before use to remove as much surface water as possible. Even so the amount of hydrogen present in ordinary quartz has been estimated[6] as 10^{19} hydrogen atoms per cm.^{3}. The number of hydrogen atoms required to produce the observed amounts of HT is less than 10^{13}. Thus it is reasonable to assume that this HT could have come from the reaction of a recoil tritium atom with hydrogen on or near the surface of the quartz.

TABLE 2

Pressure of C_2D_6	72	8·0	3·9	1·09
Pressure of ^3He	1	2·0	2·0	2·25
Pressure of O_2	3	1·0	0·4	4·45
Pressure of ^4He	0	0	0	61·2
HT	Trace	61	137	278
DT	172	233	283	690
CD_3T	9·7	9·6	11·0	11·3
C_2D_5T	100	100	100	100
C_2D_3T	~4	Trace	Trace	Trace

At low pressure the DT/C_2D_5T ratio is still higher than at high pressures. This might be due to recoil tritium atoms reacting with deuterated fragments that become adsorbed on the surface of the quartz during the reaction.

It appears from this work that any results from highly moderated systems[3,4] should be treated sceptically and wall effects considered before 'trends' are interpreted exclusively in terms of hot atom reactions.

(*Received, February 26th*, 1965.)

[3] A. H. Rosenberg and R. Wolfgang, *J. Chem. Phys.*, 1964, **41**, 2159. D. S. Urch and M. J. Welch, Proc. of Symposium on Chem. Effects associated with Nuclear Reactions and Radioactive Transformations, I.A.E.A. (Vienna), 1965.
[4] P. J. Estrup, Ph.D. Thesis, Yale University, 1959.
[5] E. H. Carter, jun., and H. A. Smith, *J. Phys. Chem.*, 1963, **67**, 1512.
[6] A. Kats, *Philips Research Report*, 1962, **17**, 201. R. A. Weeks and M. Abraham, *J. Chem. Phys.*, 1965, **42**, 68.