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HOT SYNTHESIS OF COMPOUNDS LABELLED WITH RADIOACTIVE TRITIUM

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1. ENERGY AND CHARGE OF TRITIUM ATOMS PRODUCED BY NUCLEAR REACTIONS†

Tritium is obtained by the reactions $^6Li(n, \alpha)T$ and $^3He(n, p)T$, the former being of practical interest. The capture cross-section of ^6Li for thermal neutrons is 945 barns, and ^6Li makes up 7.5% of the mixture of lithium isotopes. The yield of tritium is calculated from the formula:

$$A = \Phi_0 (1 - e^{-n\sigma x}) \lambda t,$$

where Φ_0 is the neutron flux, σ is the cross-section of the nuclear reaction, n is the number of atoms per cm^3, x is the thickness of sample, t is the period of irradiation, and λ is the decay constant. The recoil tritium atoms obtained by the reaction $^6Li(n, \alpha)T$ have energy 2.73 MeV and free path in the condensed phase of $\sim 50\ \mu$ (5 mg cm^{-2}). The recoil tritium atoms produced by the reaction $^3He(n,p)T$ only have energy 0.192 MeV.

Chemical reactions become possible when the recoil atoms have sufficient kinetic energy so that after collision with a molecule they can form a stable bond with an atom of this molecule. With comparatively low energies the reaction between the recoil atoms and the molecule passes through a transition complex in which the excess energy is evenly distributed among all the degrees of freedom, and which as a result of concentration of the necessary energy at one of the bonds decomposes to form the reaction products. As the energy of the recoil atom increases, the probability of forming the transition complex will decrease. Kinetics are normally concerned with the minimum energy required for a reaction and with the direction of the reaction at a given energy. A feature of the kinetics of the reactions of recoil atoms is that they relate to chemical reactions of large energies.

Collisions which can produce chemical reactions will occur when the recoil atom has the maximum possible energy to allow for stabilisation of the tritium bond in the molecule. If the tritium atom has a greater energy, then on collision it will not enter into the reaction, and if after

† These atoms will subsequently be called recoil tritium atoms.

subsequent collisions it has energy less than the bond energy, then it may reach thermal energies and react as a thermal atom. The latter will only occur if the probability of reaction on collision and the number of collisions in the high-energy region are sufficiently low.

The conditions for reactions to proceed at the maximum permissible energy are greatly different from the conditions for low energies. Limitations associated with the energy of activation become less important, since normally there is always an excess of energy; moreover the direction of reaction is no longer controlled by the path of minimum energy, and the reaction can proceed much more rapidly and in several directions. As the excess of energy increases, the assumed equilibrium distribution of energy throughout the whole molecule becomes less and less probable. At very high energies, although the tritium atom forms a "complex" when it collides with a molecule, there may not be any equilibrium distribution of energy throughout the whole molecule, and it is possible that only part of the molecule will participate in substitution or other reactions, independently of the remainder of the "complex", the time required for the reaction being of the same order as, or less than, the period of vibration of a single bond. There is apparently also an intermediate region of energies where part of the excess energy is distributed throughout the whole molecule; in this case the energy of activation will have only a partial influence on the direction of reaction.

If we had accurate information on the reactions of particles of high kinetic energy, we could construct a graph of probability of reaction against energy of particle, and calculate the total probability of formation of any molecule as a function of particle energy. Fig. 1 shows such a hypothetical curve for recoil tritium atoms. The probability of any reaction is zero at energies below the energy of activation, and also at high energies when the tritium atom cannot form a stable bond on collision with a molecule. The maximum probability of reaction, the width of the high-energy sector, and the shape of the curves are generally unknown. It can be qualitatively deduced from Fig. 1 that reaction *I* will have a much greater velocity for thermal atoms than reaction *II*, because of the low energy of activation. At high recoil atom energies the rates of these reactions will be approximately the same.

According to some data, however[3,10], the initial energy of the recoil atoms has no effect on the distribution of tritium among the reaction products. Thus the yields of active products obtained from methane and recoil tritium atoms produced by the reactions $^6Li(n, \alpha)T$ and $^3He(n, p)T$ are almost the same, 49.0% and 50.0% for HT and 30.5% and 31.8% for CH_3T respectively[1-3]. Consequently the chemical reactions of recoil atoms commence after they have cooled to energies of the order of a few electron-volts.

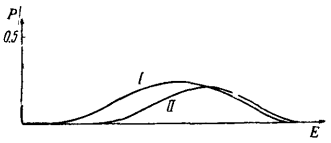


Fig. 1. Efficiency of collisions of recoil tritium atoms with organic molecules as a function of the kinetic energy of the tritium atoms (hypothetical curve).

At the time of its formation the recoil tritium atom has a positive charge; as it is then slowed down in the medium there is repeated rearrangement of charge, and most of the recoil tritium atoms of energy of a few electron volts are neutralised[3-6]. Hence it is mainly uncharged tritium atoms which take part in reactions.

To obtain organic compounds labelled with tritium a mixture of a finely-ground solid insoluble lithium salt with solid or liquid organic compounds is irradiated; or the lithium salt may be dissolved in the organic substance. On irradiation of a mixture of organic compound and lithium carbonate the specific gravity of the parent compound is calculated from the formula[7]:

$$\beta = 10^3 KRPnt,$$

where R is the percentage introduction of tritium into the irradiated compound, P the percentage of lithium carbonate in the mixture, n the neutron flux per cm^2 per sec, t the duration of irradiation in sec, and K a constant.

With $n = 10^{12}$, irradiation for 24 h can give a specific activity of the order of 10^5–10^6 disintegrations per sec, per mg. The chemical nature of the lithium compounds used to obtain the recoil tritium atoms has no influence on the distribution or yield of the tritium reaction products[11].

2. REACTIONS OF RECOIL TRITIUM ATOMS

Tables 1, 2, and 3 show published data on the distribution of tritium when the recoil atoms react with various compounds.

TABLE 1. Products of the reaction of recoil tritium atoms, obtained by the reaction $^3He(n,p)T$, with gaseous organic compounds. In cases marked* the tritium is obtained by the reaction $^6Li(n,\alpha)T$ in the liquid phase.

System irradiated	Flux, neutrons per cm^2 per sec	Period of irradiation	Active reaction products, %							Ref.
			H_2	CH_4	C_2H_6	$C_2H_4+C_2H_2$	C_3H_8	C_3H_6	C_4H_{10} and higher	
CH_4	$5\cdot10^{12}$	10 min	50.0	31.8	7.7	—		10.4		3
	$2\cdot10^9$	96 h	61.7	29.8	2.6	—		5.4		
	$3\cdot10^{13}$	1 h	46.0	31.0	6.8	—		14.2		4
	$1.2\cdot10^{13}$	2 min	53.5	32.5	—	14.0				7
	$3\cdot10^{12}$	1 h	51	33	7.4	—		8.9		10
	$5\cdot10^{12}$	—	49.0	30.5	11.2	—		9.3		10
CH_4*	$5\cdot10^{12}$	30 sec	39.1	48.6	5.5	0.3		6.5		9
CH_4+I_2	$4\cdot10^{12}$	20 min	28.2	27.5	0.1	—		0.4		3
	$3\cdot10^{13}$	1 h	40	50	trace	—		trace		2
CH_4+NO	$1\cdot10^{13}$	2 min	31.5	36.5		<1				2
$CH_4+C_2H_4$	$3\cdot10^{12}$	1 h	28	24	6.3	3.2	14	—	24.1	10
CH_4+H_2(13%)	$3\cdot10^{12}$	1 h	75	20	3.0	—		2.3		10
C_2H_6	$5\cdot10^{12}$	20 min	43.4	3.8	27.5	—	9.7	—	15.3	3
C_2H_6	$3\cdot10^{12}$	1 h	43	5	28	—	9.0	—	14.0	2
	$3\cdot10^{12}$	1 h	60	3.2	25	—	5.1	—	7.1	10
C_2H_6*	$5\cdot10^{12}$	30 sec	41.7	5.4	37.5	4	5.3	—	6.2	2
$C_2H_6+I_2$	$4\cdot10^{12}$	20 min	40.0	3.6	22.3	—	0.8	—	3.8	3
$C_2H_6+Br_2$	$3\cdot10^{13}$	1 h	42	2.0	37.0	—	—	—	—	2
$C_2H_6+C_2H_4$(10%)	$3\cdot10^{12}$	1 h	36	2.4	26	3.7	7.7	—	23.1	10
$C_2H_6+^4He$	$4\cdot10^{12}$	1 h	58.8	2.8	11.8	—	7.8	—	18.5	3
C_2H_4	$3\cdot10^{13}$	1 h	16	0.2	2.3	53	1.8	—	26.3	10
$C_2H_4+O_2$	$1\cdot10^9$	—	18	trace	79.0	3.9	—	trace	—	10
C_3H_8	$3\cdot10^{12}$	1 h	61	2.5	2.4	—	26	—	8.2	10
	$3\cdot10^{12}$	1 h	43	4	2.5	—	36.0	—	14.5	2
	$5\cdot10^{12}$	5 min	66.2	3.2	2	1.4	23.0	0.5	3.2	2
	$1\cdot10^{13}$	12 h	62.1	5.7	4.4	0.4	21.1	0.4	5.9	11
$C_3H_8+Br_2$	$3\cdot10^{12}$	1 h	50.0	3.0	1.5	—	39.0	0.5	—	11
$C_3H_8+C_2H_4$	$3\cdot10^{12}$	1 h	41	3.0	5.2	2.5	25		23.6	10
C_3H_8	$2\cdot10^9$	40 h	31.2	1.2	—	13	4.5	41	8.2	11
	$3\cdot10^9$	144 h	29.6	1.3	—	13.8	3.7	41.7	8.6	11
	$1\cdot10^{12}$	12 h	50	3.5	0.5	1.3 11.5	4.6	25.7	3.6	11
$C_3H_8+O_2$	$1\cdot10^9$	—	36.0	2.0	—	1.5 15.0 2.0	1.0	44.0	—	10

TABLE 2. Products of the reaction of recoil tritium atoms, obtained by the reaction $^3He(n,p)T$ with gaseous organic compounds.

System irradiated	Flux, neutrons per cm^2 per sec	Time, h	Active products, %												
			H_2	CH_4	C_2H_6	$C_2H_4 + C_3H_8$									
	$1 \cdot 10^9$	138	31.2	2.5	6.2	1.5	12.0	22.1	2.1	3.0	8.6				
+NO	$1 \cdot 10^9$	138	52	1	—	2.3	—	37.5	6	3.5	. . .				
+He^4	$1 \cdot 10^9$	138	31.0	1.9	8	2.3	13	11.4	1.8	—	27.9	....			
	—	—	62.3	4	4	1.3	1.6	—	0.3	—	26.5				
	$1 \cdot 10^{12}$	12	47	3.4	0.3	3.5	0.9	—	11.9	8.3		2.6	11.9	6.4	
+He^4	$2 \cdot 10^9$	48	42.6	1.5	2		—	—	14.7	7.2		2.5	21.2	1.7	
+NO	$2 \cdot 10^9$	48	43	2.1	1.2		—	—	17.1	—	—	12	22.6	3.8	
	$1 \cdot 10^{12}$	12	55.6	1.2	5.5		1.1	—	11.2	—	—	2.9	2.6	11.3	
+O_2	$1 \cdot 10^9$	168	47	2.1	2.3		—	—	17.6	—	—	2.4	1.6	26.8	
	—	—	37.3	3.4	0.8	10.4	—	—	10.4	7.8		26	1.8	1	
+O_2	—	—	39.2	2	12.5	0.6	—	—	13.4	—	—	29.1	1.1	0.9	
	$1 \cdot 10^9$	168	45	3.5	trace		—	—	8.2	3.9	—	—	—	—	39
	$1 \cdot 10^9$	168	43.7	2.2	1.5	8.1	0.7	—	10.3	—	—	1.0	—	—	—
	$1 \cdot 10^9$	168	47.5	3.3	0.5	1.5	—	—	6.0	—	—	6.0	0.5	trace	—
	$1 \cdot 10^9$	168	44.0	3.0	—	1.0 1.0	trace	—	5.0	—	—	2.0	trace		10.0
	$1 \cdot 10^9$	168	34.0	5.5	0.2	9.0	0.5	—	0.7	—	—	0.9	5.4	3.5	trace
	$1 \cdot 10^9$	168	49.0	3.6	trace	0.4	—	—	0.4	—	—	0.4	3.6	2.1	7.2
	$1 \cdot 10^9$	168	61.0	3.6	—	trace	—	—	0.9	—	—	—	—		
	$1 \cdot 10^9$	168	55.4	2.0	0.7	8.8	1.0	—	10.5	—	0.6	1.2	—		—
	$1 \cdot 10^9$	168	56.4	2.4	1.2	1.8	0.3	—	6.3	—		4.5	0.3	trace	—

TABLE 2 (contd).

System irradiated	Flux, neutrons per cm^2 per sec	Time, h	Active products, %												Ref.
															
	$1 \cdot 10^9$	138	7.5	.....											12
+NO	$1 \cdot 10^9$	138													12
+He^4	$1 \cdot 10^9$	138													12
	—	—													13
	$1 \cdot 10^{12}$	12	1.2	.....											11
+He^4	$2 \cdot 10^9$	48													10
+NO	$2 \cdot 10^9$	48													11
	$1 \cdot 10^{12}$	12	9.3	.....											11
+O_2	$1 \cdot 10^9$	168													10
	—	—													13
+O_2	—	—													10
	$1 \cdot 10^9$	168													10
	$1 \cdot 10^9$	168	5.9	24.8	2.0										10
	$1 \cdot 10^9$	168	7.7	1.5	25.8										10
	$1 \cdot 10^9$	168	4.0	—	—	28.0	2.0								10
	$1 \cdot 10^9$	168	16.0	—	—	—	0.5	24.0							10
	$1 \cdot 10^9$	168	7.6 *	—	—	3.2	21.0	1.0							10
	$1 \cdot 10^9$	168	—	—	—	—	8.0	—	8.0	14.5	4.0				10
	$1 \cdot 10^9$	168	—	0.9	—	—	—	—	2.1	—	—	1.8	1.5		10
	$1 \cdot 10^9$	168	—	0.4	0.3	—	—	—	4.5	—	—	15.0	1.8	1.8	10

TABLE 3. Products of the reaction of recoil tritium atoms obtained by the reaction $^6Li(n,\alpha)T$ with solid and liquid organic compounds.

Compound irradiated	Flux, neutrons per cm^2 per sec	Period of irradiation	Active products	Radiochemical yield, %	Specific activity, $\mu c/g$	Ref.
Benzene + Li_2CO_3	$3–4\cdot10^{12}$	30 min	benzene	26	28	16
			cyclohexa-1,4-diene	2.5		
			cyclohexa-1,3-diene	1.2		
			linear C_6	0.3		
Benzene-d_6 + Li_2CO_3	$3–4\cdot10^{12}$	30 min	benzene-d_6	24.2	26	16
			cyclohexa-1,4-diene	2.6		
			cyclohexa-1,3-diene	1.1		
			linear C_6	0.2		
Benzene + LiC_2H_5	$3–4\cdot10^{12}$	30 min	benzene	52	1.7	16
			cyclohexa-1,4-diene	5.2		
			cyclohexa-1,3-diene	2.6		
			linear C_6	1		
Benzene clathrate	$3–4\cdot10^{12}$	30 min	benzene	42.5	100	16
			cyclohexa-1,4-diene	trace		
			cyclohexa-1,3-diene	trace		
Cyclohexane	$3–4\cdot10^{12}$	30 min	cyclohexane	10	8	17
Cyclohexene	$3–4\cdot10^{12}$	30 min	cyclohexene	11	10	17
			cyclohexane	9	90	17
Cyclohexa-1,4-diene	$3–4\cdot10^{12}$	2 h	cyclohexa-1,4-diene	17	60	17
			cyclohexa-1,3-diene	5	65	17
			cyclohexene	15	330	17
			benzene	29	60	17
Cyclohexa-1,3-diene	$3–4\cdot10^{12}$	2 h	cyclohexa-1,3-diene	3.3		17
			cyclohexa-1,4-diene	2.6		
			cyclohexene	14.1		
			benzene	29.0		
Methylcyclohexane(liq.) $C_6H_{11}CH_3$	$4\cdot10^{12}$	5 h	$H_2 + CH_4$	60.9		17
			C_6H_{12}	3.9		
			$C_6H_{11}CH_3$	35.2		
Cyclohexanol(liq.) $C_6H_{11}OH$	$4\cdot10^{12}$	5 h	$H_2 + CH_4$	66.3		17
			C_6H_{12}	3.9		
			$C_6H_{11}OH$	29.8		
Cyclohexylamine $C_6H_{11}NH_2$	$4\cdot10^{12}$	5 h	$H_2 + CH_4$	61.9		
			C_6H_{12}	5.3		
			$C_6H_{11}NH_2$	32.8		
$C_6H_5CH_3$	$9\cdot10^{11}$	97 h	$C_6H_5CH_3$	40	220	18
CH_3OH(liq.)	$1.8\cdot10^{12}$	1 h	CH_3OH	23	1.3	19
C_2H_5OH(liq.)	$1.8\cdot10^{12}$	2 h	H_2	51.4		19
			CH_4	3.5		
			$C_2H_4 + C_2H_6$	1.7		
			$C_3H_8 + C_4H_{10}$	0.4		
			C_2H_5OH and other liquid products	20	2.2	
				23		
CH_3COCH_3(liq.)	$1.8\cdot10^{12}$	2 h	CH_3COCH_3	24	2.9	19
			CH_3CHO	9.1		
CH_3COCH_3(solid)	$4\cdot10^{12}$	1 h	CH_3COCH_3	24	3.6	19
			CH_3CHO	5		
			iso-C_3H_7OH	1.7		
CH_3COCH_3(liq.) + 30% H_2O	$1.8\cdot10^{12}$	1 h	CH_3COCH_3	25	1.2	19
			CH_3CHO	7.5		
L(+)-$CH_3CH(NH_2)COOH$, 14% aq. soln.	$1.8\cdot10^{11}$	24 h	*dl*-$CH_3CH(NH_2)COOH$	$\geqslant 0.5$		20
L(+)-$CH_3CH(NH_2)COOH$ (solid)	$1.8\cdot10^{12}$	24 h	*dl*-$CH_3CH(NH_2)COOH$	$\geqslant 12$		20
dl-Threonine	$2.5\cdot10^{11}$	17 h	*dl*-threonine	–	82	42
			allothreonine	–	108	
			glycine	–	11	
Glucose(solid)	$6\cdot10^{9}$	65 h	glucose	10	3	21
Glucose(solid)	$1.8\cdot10^{12}$	24 h	glucose	22	266	22
Glucose, 48% aq. soln.	$1.8\cdot10^{12}$	24 h	glucose	1	1.7	22
Galactose(solid)	$1.8\cdot10^{12}$	27 h	galactose	12	11.3	21
$C_6H_5COOC_3H_7$	$1\cdot10^{12}$	118 h	$C_6H_5COOC_3H_7$	16.8	0.188	23
$C_6H_5COOC_3H_7$	$1\cdot10^{12}$	153 h	$C_6H_5COOC_3H_7$	10.2	0.217	23
C_6H_5COOH	$1\cdot10^{12}$	72 h	C_6H_5COOH	25	90	24
C_6H_5COOH	$1\cdot10^{12}$	168 h	C_6H_5COOH	16	150	25
o-, *m*-, *p*-$NH_2C_6H_4COOH$	$5\cdot10^{12}$	2 h	$NH_2C_6H_4COOH$	32–35	21.7	26
o-, *m*-, *p*-$NO_2C_6H_4COOH$	$5\cdot10^{12}$	2 h	$NO_2C_6H_4COOH$	27–29	1.6	26
o-, *m*-, *p*-HOC_6H_4COOH	$5\cdot10^{12}$	2 h	HOC_6H_4COOH	43–31	26.7	26
o-, *m*-, *p*-$C_6H_4(COOH)_2$	$5\cdot10^{12}$	2 h	$C_6H_4(COOH)_2$	32	20	26
o-, *m*-, *p*-BrC_6H_4COOH	$5\cdot10^{12}$	2 h	BrC_6H_4COOH	36–42	26.7	26
o-, *m*-IC_6H_4COOH	$5\cdot10^{12}$	2 h	IC_6H_4COOH	33–36	23.3	26
o-, *m*-FC_6H_4COOH	$5\cdot10^{12}$	2 h	FC_6H_4COOH	44–57	36.7	26
o-, *p*-ClC_6H_4COOH	$5\cdot10^{12}$	2 h	ClC_6H_4COOH	42–49	31.7	26
Phenylpropionic acid	$5\cdot10^{12}$	2 h	phenylpropionic acid	35	23.3	25
Maleic acid	$5\cdot10^{12}$	2 h	maleic acid	10	6.7	25
Fumaric acid	$5\cdot10^{12}$	2 h	fumaric acid	12	8.3	25
cis-Cinnamic acid	$5\cdot10^{12}$	2 h	*cis*-cinnamic acid	15	10	25
trans-Cinnamic acid	$5\cdot10^{12}$	2 h	*trans*-cinnamic acid	30	18.3	25
trans-Cinnamic acid Na salt	$1.3\cdot10^{12}$	8 h	*trans*-cinnamic acid Na salt + *trans*-cinnamic acid	27	20	25
Acetic acid	$1.7\cdot10^{12}$	1 h	acetic acid	18	1.7	27
			H_2	33		
			CH_4	13		

TABLE 3 (contd).

Compound irradiated	Flux, neutrons per cm^2 per sec	Period of irradiation	Active products	Radiochemical yield, %	Specific activity, $\mu c/g$	Ref.
Propionic acid	$2–4\cdot10^{12}$	1 h	propionic acid	22		27
			H_2	43		
			CH_4	2.1		
			C_2H_6	7.5		
n-Butyric acid	$2–4\cdot10^{12}$	1 h	n-butyric acid	27		
			H_2	49		
			CH_4	2.6		
			C_3H_8	3.7		
Isobutyric acid	$2–4\cdot10^{12}$	1 h	isobutyric acid	26		27
			H_2	47		
			CH_4	4.7		
			C_3H_8	3.3		
n-Valeric acid	$2–4\cdot10^{12}$	1 h	n-valeric acid	20		27
			H_2	65		
			CH_4	2.0		
			C_4H_{10}	2.2		
Isovaleric acid	$2–4\cdot10^{12}$	1 h	isovaleric acid	33		27
			H_2	48		
			CH_4	4.5		
			iso-C_4H_{10}	2.1		
t-Valeric acid	$2–4\cdot10^{12}$	1 h	t-valeric acid	20		27
			H_2	43		
			CH_4	9.6		
			s-C_4H_{10}	6.8		
n-Caproic acid	$2–4\cdot10^{12}$	1 h	n-caproic acid	27		27
			H_2	46		
			CH_4	1.3		
			C_5H_{12}	0.9		
t-Caproic acid	$2–4\cdot10^{12}$	1 h	t-caproic acid	33		27
			H_2	34		
			CH_4	2.8		
			s-C_5H_{12}	0.8		
Phenylacetic acid	$7\cdot10^{12}$	2 h	$C_6H_5CH_2COOH$	30	33	28
Nicotinic acid	$2\cdot10^{13}$	48 h	nicotinic acid	6	150	29
Nicotinic acid	$1\cdot10^{12}$	72 h	nicotinic acid	23	100	30
o-Toluidinic acid	$1\cdot10^{12}$	72 h	*o*-toluidinic acid	25	100	30
Salicylic acid	$1\cdot10^{12}$	72 h	salicylic acid	31	100	30
Dimethyl ether	$3\cdot10^{12}$	48 h	H_2	77		31
			CH_4	4		
			CH_3OCH_3	16		
			$C_2H_5OCH_3$	3.2		
H_2O(liq.)	$2\cdot10^{9}$	144 h	H_2	10		35, 38
			H_2O	90		
H_2O(gas)	$2\cdot10^{9}$	144 h	H_2	4		35, 38
			H_2O	96		
H_2O(gas) + ^4He	$2\cdot10^{9}$	144 h	H_2	2		35, 38
			H_2O	98		
H_2O(gas) + NO	$2\cdot10^{9}$	144 h	H_2	4		35, 38
			H_2O	96		
H_2O(gas) + O_2	$2\cdot10^{9}$	144 h	H_2	1.5		35, 38
			H_2O	98.5		
Methyl *α*-glucoside	$2\cdot10^{12}$	24 h	methyl *α*-glucoside		100	7
2-Methyl-2-n-propyl-propyne-1,3-diol dicarbonate	$2\cdot10^{12}$	72 h	2-methyl-2-n-propyl-propyne-1,3-diol carbonate	6	50	7
Glucose diacetone	$2\cdot10^{12}$	24 h	glucose diacetone		100	7
Glucose diethyl-mercaptal	$2\cdot10^{12}$	24 h	glucose diethyl-mercaptal		100	7

Table 1 shows that 10–50% of the tritium forms a labelled parent molecule, 30–50% is obtained as HT molecules, and 5–25% appears as organic compounds more complex or simpler than the mother compound.

The gaseous reaction products from hot tritium atoms are qualitatively similar for most substances, while the liquid products depend on the structure of the parent molecule, the composition of the irradiated mixture, and the irradiation conditions.

The reactions of various classes of organic compound with recoil tritium atoms have been studied: saturated, unsaturated, and aromatic hydrocarbons[10,12,16], alcohols[19], ketones[19], esters[23], carboxylic acids[27], and other compounds[7,22,25,26]. The same types of reaction were observed with all these compounds. Data on the influence of radical

acceptors indicate that for most of the systems studied more than half of the recoil tritium atoms enter into reaction even in the high-energy region.

We shall now consider the types of reaction of recoil tritium atoms with organic compounds, using butane as an example, in decreasing order of probability.

Hydrogen Abstraction

This reaction proceeds mainly in the high-energy region, since the yield does not greatly depend on the presence of a radical acceptor; it also partly proceeds with thermal tritium atoms.

$$T^* + CH_3CH_2CH_2CH_3 \rightarrow \begin{matrix} CH_3CH_2\dot{C}HCH_3 \\ CH_3CH_2CH_2\dot{C}H_2 \end{matrix} + HT.$$

The formation of HT is also possible as a result of intramolecular elimination of hydrogen from an excited molecule.

Hydrogen Replacement

This reaction is insensitive to the presence of a radical acceptor, so that the parent molecule, as a rule, retains its configuration.

$$T^* + CH_3CH_2CH_2CH_3 \rightarrow \begin{matrix} CH_3CH_2CHTCH_3 \\ CH_3CH_2CH_2CH_2T \end{matrix} + H$$

The substitution reaction does not depend on the phase in which the recoil hydrogen atoms are stabilised. The determination of the intramolecular and intermolecular distribution of tritium in a system having hydrogen atoms in various positions shows that substitution occurs at all types of carbon–hydrogen bond in saturated, unsaturated, and aromatic compounds, etc. The substitution of hydrogen proceeds in random fashion in all positions; any variation in the specific activity of a given position is the result of the particular properties of the given molecule, for example, the *ortho*-position of *cis*-cinnamic acid has a lower activity than the same position in *trans*-cinnamic acid[25].

Where the tritium atom can react with hydrogen adjacent to either saturated or an unsaturated carbon–carbon bond, it reacts with about the same probability in each position[42], whereas for thermal hydrogen atoms there is a large difference in the rates of these reactions. The substitution of hydrogen atoms in organic molecules by tritium has high probability. The efficiency of a collision, as evaluated by Wolfgang, is several orders greater than than of collisions in thermal reactions which also demonstrates that these reactions occur in the high-energy region. However, the substitution reactions involving recoil tritium atoms do not take place by elastic collisions[48], as is seen by the relative amounts of tritiated methane obtained from CH_4 and CD_4.[32]

The substitution by recoil tritium atoms is a fast step in the reaction (10^{-14} sec), taking place in a time comparable with the period of vibration of the bond, and there is not always time for the excitation to be spread throughout the molecule; consequently there is local bond rupture only, and in most cases the configuration of the molecule is retained[20,22,23,45,46]. The attack by a recoil tritium atom on a hydrocarbon molecule, as already stated, may produce excitation of only part of the molecule; if the attack is along the line of a C–H bond or at a small angle to it and produces rupture of the C–H bond, the tritium atom combines with the hydrogen to form HT; if the direction of attack forms a large angle to the line of the C–H bond, the product after bond rupture will be RT.[32]

An empirical formula has recently been derived[32,34] for calculating the relative proportions of products obtained by reactions of types *I* and *II* involving aliphatic hydrocarbons.

Substitution of a Group of Atoms

This reaction produces degradation products from the original substance in yields which also do not depend on the presence of a radical acceptor:

$$T^* + CH_3CH_2CH_2CH_3 \rightarrow \begin{matrix} CH_3T \\ CH_3CH_2T \\ CH_3CH_2CH_2T \end{matrix}.$$

The replacement of a radical is less probable than replacement of hydrogen. After rupture of the C–C bond the tritium is more likely to combine with the simpler radical; a possible explanation of this has been given[47]. The yield of RT depends on the number of R groups in the irradiated compound; thus the yield of CH_3T is greater with neopentane than with isopentane, greater with the latter than with n-pentane, and least with cyclopentane.

The recoil tritium atoms can replace other atoms and groups in addition to H and CH_3; thus they readily replace $-NO_2$, $-NH_2$, $-COOH$, and $-OH$ groups and halogen atoms in corresponding benzoic acid derivatives[26].

Sometimes, it can be assumed that the substitution of a group of atoms is a secondary process. The replacement of hydrogen in the parent molecule by a recoil tritium atom produces an excited molecule, which decomposes with elimination of a group of atoms; for example, in the reaction of recoil tritium atoms with carboxylic acids an excited molecule is formed as an intermediate and then decomposes:

$$T^* + CH_3COOH \rightarrow \begin{matrix} CH_2TCOOH^* + H \\ \downarrow \\ CH_3T + CO_2 \end{matrix}.$$

The yield of decomposition products decreases as the carbon chain length is increased, because the excitation is extinguished within the molecule[8,27,37].

It has been shown[26,49,56] that in some cases the yield of labelled substitution products depends on the energy of the C–X bond, increasing with decreasing stability of the bond.

Substitution of Two Groups of Atoms

This reaction produces a labelled radical:

$$T^* + CH_3CH_2CH_2CH_3 \rightarrow \begin{matrix} CH_3CH_2CH_2\dot{C}HT + H_2 \\ CH_3CH_2\dot{C}HT + CH_3 + H \end{matrix},$$

and can give either two hydrogen atoms or one hydrogen atom and an alkyl group by elimination from the parent molecule. The radical produced may be captured by a radical acceptor, or in the absence of the latter it may decompose to a smaller radical and an alkene, by rupture of a C–C bond.

Low yields of products are usually obtained in this reaction[34,35].

TABLE 4. Introduction of recoil tritium atoms into cyclic hydrocarbons (flux: 4×10^{12} neutrons per cm^2 per sec); activity of parent compound taken as 100. Period of irradiation 5–10 h in the presence of Li_2CO_3.

Substance irradiated	Activity of reaction products, %							
	cyclohexane	cyclohexene	cyclohexa-1,4-diene	cyclohexa-1,3-diene	benzene	methylcyclohexane	methylcyclopentane	hexenes and hexanes
Cyclohexane	100	5	—	—	2	5	6	25
Cyclohexene	71	100	—	—	5	—	19	24
Cyclohexa-1,4-diene	39	92	100	32	175	—	—	—
Cyclohexa-1,3-diene	30	425	80	100	875	—	—	—
Benzene	—	1	11	5	100	0	0	0

TABLE 5. The fractions of recoil tritium atoms reacting with alcohols and acetone by the various types of reaction.

Type of reaction	Activity, %, as:		
	C_2H_5OH	CH_3OH	$(CH_3)_2O$
Replacement of inactive hydrogen by tritium	22	23	25
Replacement of labile hydrogen by tritium	20	29	12
Replacement of a methyl group by tritium	1	—	9
Formation of aldehyde from alcohol	2	1	—
Formation of aldehyde from acetone	—	—	1

TABLE 6. Yield of labelled products in the reaction of recoil tritium atoms with alkanes (yield of labelled parent compound taken as unity).

Labelled compound	Type of reaction	Starting compound								
		methane	ethane	propane	n-butane	isobutane	n-pentane	isopentane	neopentane	n-hexane
HT	H abstraction	1.0	1.82	1.97	1.99	1.92	2.37	2.03	1.40	3.28
Parent compound	H replacement	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Lower alkanes	replacement of alkyl group	—	0.12	0.15	0.15	0.17	0.19	0.21	0.23	0.31
Methyl iodide (initially CH_2T) in the presence of iodine	replacement of an alkyl group + H or + 2H	0.12	0.14	0.06	0.09	0.05	0.08	0.09	0.09	0.07
Alkene (initially a radical)	replacement of an alkyl group + H	—	0.11	0.08	0.08	0.09	0.10	0.09	0.05	0.12
Isomerisation and other products	–	—	0.03	0.00	0.01	0.01	0.00	0.00	0.01	0.02

Addition Reactions

A labelled radical is also produced in the reaction of recoil tritium atoms with unsaturated hydrocarbons:

$$T^* + R{-}CH_2{-}CH{=}CH{-}CH_2{-}R' \rightarrow R{-}CH_2{-}\dot{C}HT{-}CH{-}CH_2{-}R'^*.$$

The resulting radicals are excited, and decompose to form two or three fragments containing less carbon atoms than the parent molecule [12,34] and which retain the structure of the parent molecule, being produced by the rupture of a single bond. The yields of all products obtained in the reaction of recoil tritium atoms with alkenes are given in Table 2; these yields confirm the mechanism postulated by Rice [51] and McNesby [52] for the decomposition of hot radicals. The yield of HT increases and the yield of parent compound decreases as the molecular weight of the alkene increases, as with the alkanes.

In the reaction of hot tritium atoms with unsaturated cyclic compounds (cyclohexene and cyclohexadienes) the main products, besides the parent compound and hydrogen, are hydrogenation products: cyclohexene gives cyclohexane, and cyclohexadienes give mainly cyclohexene.

The probability of rupture of a C–C bond by addition of a recoil tritium atom to a double bond is lower in the case of cyclohexene and cyclohexadienes than with open-chain alkene (Table 4) [17].

Cyclohexadienes also give labelled benzene in large amount, a large quantity of benzene being obtained by radiolysis of the cyclohexadienes.

Recoil tritium atoms can also add to aromatic bonds [16], benzene producing a labelled cyclohexadiene radical which is subsequently converted into cyclohexa-1,4- or cyclohexa-1,3-diene. Since these compounds are formed without radiolytic carriers, they have a high specific activity and their production is of considerable interest. Compounds produced by opening of the benzene ring are obtained in very low yield (Table 4).

The relative yields of products obtained from alkanes, alcohols, and acetone by the various types of reaction are shown in Tables 5 and 6.

3. INFLUENCE OF VARIOUS FACTORS ON THE YIELD OF LABELLED COMPOUNDS

Influence of Radical Acceptors

Radical acceptors normally used in the gas phase are iodine vapour, bromine vapour, nitric oxide, oxygen, etc. Table 7 relates to the reaction of methane with recoil tritium atoms, and shows that these radical acceptors have the same efficiency [9].

It is seen from Table 7 that even small amounts of the radical acceptors have a large effect on the yields of the individual products. In the presence of radical acceptors at pressure above 1 mm the yield of labelled hydrocarbons of higher molecular weight than methane (*e.g.* ethane, propane, and butane) falls sharply, while the yield of labelled methyl halide remains constant. The presence of radical acceptors has no marked influence on the yield of labelled methane. The yield of HT first falls sharply, then with a pressure of radical acceptors > 1 mm falls very slowly. Similar effects are given by oxygen in the reaction of recoil tritium atoms with dimethyl ether [4].

The influence of iodine concentration on the yield of labelled products when liquid acetic acid is irradiated has been studied [27]. The tritium distribution in the gaseous products is almost independent of the iodine concentration when the latter is below 10^{-4}; with high iodine concentrations, the yield of hydrocarbons other than methane is markedly less, but does not fall to zero. Even with an iodine concentration as high as 10^{-2} M, when the iodine

TABLE 7. Reaction of recoil tritium atoms with methane in the presence of radical acceptors.

Radical acceptor	Temperature, °C	Pressure of radical acceptor	Yield of labelled products, %			
			HT	CH_3T	CH_2TX	$>C_1$
	above room temp.	0	0.535	0.325	0	0.14
Br_2	~ −100	~0.01	0.42	0.32	0.018	0.11
Br_2	~ −60	~0.6	0.37	0.345	0.042	0.015
I_2	above room temp.	~1	0.35	0.32	0.020	<0.01
Br_2	~ −45	2—2	0.32	0.36	0.037	<0.01
NO	above room temp.	~9	0.315	0.365	...	<0.01
Br_2	~ −15	~20	0.29	0.33	0.045	<0.01
Br_2	above room temp.	>20	0.23	0.30	0.042	<0.01

remains in the free state even after the irradiation, a considerable amount of ethane is formed, apparently because some of the radicals leave the liquid phase for the gaseous phase, where they are stabilised by the addition of hydrogen atoms to form stable chemical compounds. The yield of labelled parent compound is independent of the iodine concentration.

When liquid benzene is irradiated together with lithium carbonate in the presence of diphenylpicrylhydrazide, the yield of labelled benzene hydrogenation products decreases with increasing concentration of the diphenylpicrylhdrazide [16].

All these examples show that the presence of radical acceptors does not as a rule affect the yield of products obtained by substitution of tritium for hydrogen or a group of atoms. However, substances of the radical acceptor type do not always decrease the yield of labelled products; for example, the yield of labelled benzene in the reaction of recoil tritium atoms with benzene is increased by about 50% in the presence of iodine [40]. The explanation given is the formation of an intermolecular benzene–iodine complex, which promotes removal of energy from the excited labelled benzene molecule. The yield of labelled benzene is shown in Fig. 2 as a function of the iodine concentration.

Sauer [10] used ethylene as radical acceptor in the reaction of recoil tritium atoms with methane, ethane, and propane; as with halogens as radical acceptors, the yield of labelled hydrogen falls. It may be assumed that the reaction of thermal tritium atoms with ethylene:

$$C_2H_4+T \rightarrow C_2H_4T,$$

will compete successfully with the hydrogen abstraction reaction:

$$T+CH_4 \rightarrow CH_3+HT.$$

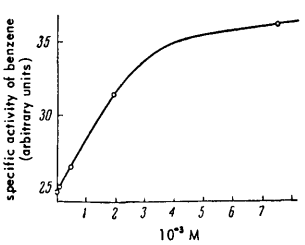


Fig. 2. Specific activity of benzene as a function of the iodine concentration.

The fact that the yield of labelled ethane from ethane and that of labelled propane from propane is unaffected by the presence of ethylene again confirms that these products are produced wholly by substitution of hydrogen in the initial molecule by a hot tritium atom. It might be expected that the presence of 8% of ethylene in the irradiation of ethane and propane would lower the yield of labelled molecules of these compounds, if only by a simple dilution effect, but in fact the yield remains constant. In this case it may be assumed that the radical C_2H_4T produced can form labelled molecules of the parent compounds, *e.g.* by the reactions:

$$C_2H_4T+C_2H_6 \rightarrow C_2H_5T+C_2H_4,$$

$$C_2H_4T+C_3H_8 \rightarrow C_2H_5T+C_3H_5,$$

and $$C_2H_4T+CH_3 \rightarrow C_3H_7T.$$

There is no reaction by which labelled methane could be produced from the ethyl radical, and therefore its yield decreases in the presence of ethylene.

Unlike halogen radical acceptors, which combine with tritium atoms to form hydrogen halides which are not detected when the irradiated mixture is analysed by gas chromatography, ethylene combines with tritium to form the radical C_2H_4T, the reaction products of which are readily detected by gas chromatography. Unlike halogens, ethylene only slightly reduces the yield of higher hydrocarbons.

Hydrogen readily enters into certain ionic-molecular reactions, and so to a certain extent can act as an ion acceptor and so hinders the formation of "higher" products. Since hydrogen is always produced in the irradiation of organic compounds, its influence must be investigated, and the system $^3He + CH_4 + H_2$ has been studied for this purpose [10]. Table 8 shows that there is no great change in the yield of labelled compounds when 20% of hydrogen is added to the methane. The cause of the reduced yield of CH_3T may be the formation of HT by reaction between hot tritium atoms and H_2, the greater retarding efficiency of H_2 as composed to CH_4, and exchange between thermal T atoms and H_2. All these factors increase the yield of labelled hydrogen. The reduction of the yield of synthesis products by half may be due to the decreased specific activity of the HT, if it is assumed that HT molecules participate in the production of more complex molecules.

TABLE 8. Influence of hydrogen on the yield of labelled products produced by irradiation of the system $^3He + CH_4 + H_2$ (yields reported as percentage of the total observed activity); partial pressure of CH_4 = 500–600 mm, partial pressure of ^3He = 6 mm.

Labelled products	Partial pressure of H_2					Labelled products	Partial pressure of H_2				
	0.3	0.9	5.3	9.3	12.3		0.3	0.9	5.3	9.3	12.3
	yield, %						yield, %				
H_2	50	52	65	75	74	C_5	0.3	0.5	0.2	0.2	0.2
CH_4	34	32	26	20	20	C_6	1.0	1.1	0.6	0.3	0.4
C_2H_6	7.5	7.4	4.1	3.0	2.8	C_6	—	0.5	0.2	—	0.2
C_3H_8	3.3	2.0	1.7	1.0	0.9	C_6	—	0.7	0.2	—	0.3
iso-C_4H_{10}	1.0	1.0	0.5	0.4	0.3	C_7	—	1.0	1.1	—	0.3
n-C_4H_{10}	1.0	1.1	0.7	0.4	0.4						

If radical acceptors are added to the system after the irradiation the yield of labelled products remains unchanged[3].

Influence of Inert Diluents

The introduction of inert substances into the organic compound–recoil tritium atom system, *e.g.* ^{4}He, Ne, Ar, Kr, etc. in the gaseous phase, suppresses the hot reactions and the only products are those of thermal processes, *i.e.* in the first instance the yield of parent compound is reduced[3,22]. The efficiency of retardation of the hot tritium atoms by the inert gases decreases on passing in the series from helium to xenon. These facts confirm that the recoil tritium atoms react with methane by "hot" reactions. The inert gases do not affect the yield of labelled products solely by the dilution effect, since with specimens containing the same molar fraction of different inert gases the yields are different, and decrease in the series Xe to He. The retarding capacity of the inert gases increases in the same series. In the reaction between recoil tritium atoms and a gaseous mixture of acetylene and propane the ratio of the specific activity of acetylene to that of propane increases linearly with the relative concentration of helium, because of thermal processes by which tritium is introduced into acetylene.

If a radical acceptor is present in addition to the retarding agent, the yield of labelled organic products is still further reduced: the yield of labelled methane from methane and recoil tritium atoms in the presence of helium and bromine is only 1%, the yield of HT is ~ 5± 5%, and higher hydrocarbons are absent[3]. The yield of higher hydrocarbons in the absence of a radical acceptor increases with decreasing molar fraction of the parent compound.

Hot tritium atoms may be slowed down by the sides of the ampoule in which the mixture is irradiated, and the dimensions of the ampoule may therefore affect the yield of labelled products. This effect was investigated by reacting recoil tritium atoms with methane in an ampoule containing quartz powder: however, the yield of labelled methane increased only to 37%,[3] which is within the limits of the experimental error (see Table 1).

The presence of quartz powder may appreciably affect the yield of labelled products in other reactions; thus the yields of individual products are greatly increased in the radiolysis of n-pentane in the presence of silica[30].

Influence of Temperature and Phase State of the Initial Compound on the Yield of Labelled Compounds

The yield of labelled products was not found to depend substantially on temperature in the range 0°–200°.[3] Further increase of temperature should affect the distribution of tritium among the labelled products, particularly when molecules larger than methane are irradiated. Thus it is known that in the radiolysis of gaseous pentane above 230° cracking occurs by chain reactions; for example, at 400° the yield of low hydrocarbons (up to C_5) is ~ 2000 moles per eV, which is ~ 10^3 times the yield at room temperature[31].

Change of the phase of the irradiated substance has no effect on the qualitative composition of the reaction products with recoil tritium atoms, but has a marked effect on their yield, as is demonstrated in the irradiation of liquid and gaseous methane and ethane (Table 1).

In the reaction of recoil tritium atoms with *trans*-but-2-ene and *trans*-hex-2-ene there is a considerable reduction in the yields of the alkene on passing from the gaseous to the liquid phase[54,55]. The yield of labelled parent molecules is also increased when cyclic hydrocarbons react with recoil tritium atoms in the liquid and solid phases[50].

In the reaction of recoil tritium atoms with gaseous, liquid, and solid acetone, the distribution of tritium among the products is independent of the phase of the acetone; however, with water the yield of labelled products is markedly different in the gaseous and liquid phases.

Substitution by hot and superthermal processes is thus the main reaction of hot tritium atoms, irrespective of the phase state of the system. In a condensed phase, however, the closer packing of the atoms and molecules enables the medium to absorb the excess of energy and motion from the activated complex obtained by collision. Moreover the radicals and atoms obtained by dissociation of the intermediate complex, which has too high an internal energy to form a stable compound directly, may be held together within a shell of surrounding molecules and so can recombine to produce the labelled compound. These effects explain the higher activity of the parent compound in the liquid phase as compared with the gaseous phase.

Passing from the liquid to the solid phase also has substantially no effect on the distribution of tritium in the products. Although the reaction mechanism in both condensed media is the same, the study of relatively more complex systems discloses some new and interesting effects. Studies of the irradiation by tritium of glucose and many larger molecules shows that about 20% of the tritium replaces hydrogen in C–H bonds of the parent molecule; hence the reactions of recoil tritium atoms in condensed systems can be considered as specific substitution or addition reactions which are more probable than random combination with radicals formed at the end of the free path. If the recoil energy at the end of the path were greater than required for hot substitution, it is difficult to see how a large molecule such as glucose would remain unchanged when the tritium atoms were introduced. These phenomena are in agreement with the calculations of Rowland and Wolfgang, who showed that recoil tritium atoms have a relatively long mean free path, and are not captured by the solvent until their energy is very low. This means that a very small number of radicals will be formed at the end of the path.

Influence of Radiolysis

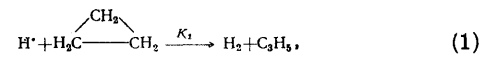
Radiolysis produces decomposition of the parent material, forming radicals and molecules of new substances, which take part in chemical reactions by which the recoil atoms are stabilised. The yield of tritium-containing products and the distribution of tritium in the molecules will thus depend greatly on the radiolysis which accompanies the stabilisation of the recoil atoms. The labelled molecules will in their turn undergo radiolytic conversions.

The source of the radiolytic action is the γ-radiation from the nuclear reactor and the recoil nuclei of hydrogen, helium, and tritium. In most cases the recoil nuclei make the most contribution; when recoil nuclei are obtained from ^{3}He each act liberates 0.765 MeV. While the accompanying γ-radiation can be varied, it is difficult to vary the effect of the recoil nuclei. The influence of radiolysis on the labelled compounds will increase with the period of

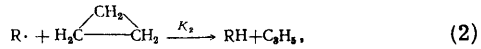
exposure to the radiation, and can be shown by varying the period of irradiation or the intensity of the neutron flux. Specimens in which the parent compound is 10–20% decomposed will have a considerable proportion of radiolytic impurities, and the tritium distribution may differ greatly from that obtained when the parent compound is only little decomposed.

In some cases this effect is particularly marked, for example with alkanes, which are fairly inert to reactions with excited atoms and radicals; the impurities formed by radiolysis will play an important part in the final tritium distribution.

Table 9 shows the variation in the distribution of activity with the period of irradiation of cyclopropane. The labelled unsaturated compounds produced by the reactions with hot tritium atoms are rapidly saturated by reaction with hydrogen atoms, and the thermal tritium atoms react preferentially with the alkenes obtained by the radiolysis of the cyclopropane. In the initial stages of irradiation the main reactions will be hydrogen abstraction reactions:

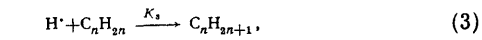


$$H^{\cdot} + H_2C(CH_2)CH_2 \xrightarrow{K_1} H_2 + C_3H_5, \quad (1)$$

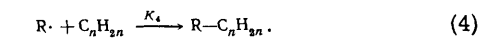


$$R^{\cdot} + H_2C(CH_2)CH_2 \xrightarrow{K_2} RH + C_3H_5, \quad (2)$$

but as time progresses the reaction products begin to build up, and can themselves react with the atoms and radicals:



$$H^{\cdot} + C_nH_{2n} \xrightarrow{K_3} C_nH_{2n+1}, \quad (3)$$



$$R^{\cdot} + C_nH_{2n} \xrightarrow{K_4} R{-}C_nH_{2n}. \quad (4)$$

The actual direction of the reaction will depend on the relative rates of the individual reactions (1)–(4) for the various radicals.

It is seen from Table 9 that the sum of the relative yields of propylene and propane remains approximately constant when the period of irradiation is varied by a factor of 70, although the individual yields are markedly different. This supports the suggestion that propylene reacts with hydrogen to form a propyl radical by reaction (3), *i.e.* saturated compounds are produced from unsaturated compounds. The total yield of ethane and ethylene is also approximately constant with different periods of irradiation.

TABLE 9. Influence of duration of irradiation on the yield of labelled products in the reaction of recoil tritium atoms with cyclopropane. The specimens contained 750 mm cyclopropane and 2 mm ^{3}He and were irradiated with a neutron flux of ~ 10^9 neutrons per cm^2 per sec. The activity of cyclopropane is taken as 100.

Period of irradiation, h	138	48	24	8	4	2	Period of irradiation, h	138	48	24	8	4	2
Percentage decomposition of initial compound	0.2	0.07	0.03	0.01	0.007	0.003	Percentage decomposition of initial compound	0.2	0.07	0.03	0.01	0.007	0.003
Labelled products	activity, %						Labelled products	activity, %					
△	100	100	100	100	100	100		13	14	16	21	7	29
HT	141	138	147	140	153	150							
CH_3T	11	9	—	—	—	—	C–C–C–C	39	30	25	15	7	9
C–C	28	22	22	16	11			30	28	26	22	—	—
C=C	7	10	10	10	12	33							
C≡C	2	2	2	—	—	—		3	4	4	3	2	—
C–C–C	54	48	44	37	20	23							
C–C=C	9	15	22	31	49	54							

Starting from the assumptions that: (*i*) hydrogen atoms and alkenes are continuously produced in the irradiation of cyclopropane; (*ii*) the alkenes disappear only by reaction with hydrogen atoms according to reaction (3) with subsequent abstraction of hydrogen atoms; and (*iii*) the hydrogen atoms are removed only by reactions (1) and (3) and rapidly reach a stationary concentration, it is possible to obtain an approximate picture of the kinetic behaviour of the atoms and radicals produced in the irradiation of cyclopropane. Using the above assumptions as a basis, it is possible to construct a curve showing the variation of the alkene concentration with the period of irradiation. The shape of this curve will depend firstly on the G-values for hydrogen and the alkenes, and secondly on the ratio K_1/K_3. The alkene concentration becomes stationary after a certain time, and since the total activity increases linearly with the period of irradiation, the fraction of the total activity contributed by the alkenes continuously decreases.

Table 10 gives the data obtained[10] on the influence of the neutron flux on the yield of labelled products in the irradiation of ^{3}He in methane, ethane, and propane. Comparison of columns A and B shows that there is no marked change in the distribution of tritium in the labelled products with a tenfold change of neutron flux at a constant total dose of irradiation. Column C gives the results of experiments in which the pressure of ^{3}He (0.1 mm) was 60 times less than in A, with the period of irradiation correspondingly 60 times more. It can be estimated that the energy distributed in the reaction vessels in unit time by recoil nuclei of tritium and hydrogen in experiments A is 30 times the energy of the γ-radiation, while in experiments C the fraction of the total energy introduced by the γ-radiation is twice that introduced by the recoil nuclei.

The intensity of the ionising radiation in experiments C was thus 20 times less than in experiments A, but the total energy absorbed in C was 3 times that absorbed in A. Under these conditions the yield of HT in the reaction of recoil tritium atoms with methane increased from 51% to 61%, while the yield of higher compounds decreased to

TABLE 10. Influence of the dose intensity and total energy absorbed from recoil nuclei and γ-rays on the yield of labelled products obtained from carrying out the nuclear reaction ^{3}He(n,p)T in methane, ethane, and propane.

Radiation conditions	Methane				Ethane				Propane		
	A	B	C	D	A	B	C	D	A	C	D
Flux, 10^{12} neutrons per cm^2 per sec	2–3	20–30	2–3	2–3	2–3	20–30	2–3	2–3	2–3	2–3	2–3
Pressure of ^{3}He, mm	6	6	0.1	6	6	6	0.1	6	6	0.1	6
Period of irradiation	1 h	10 min	60 h	3 min	1 h	10 min	60 h	3 min	1 h	60 h	3 min
Labelled products	%				%				%		
H_2	51	51	61	65	60	57	63	70	61	62	75
CH_4	33	32	36	29	3.2	3.9	3.7	3.5	2.5	3.0	2.0
C–C	7.4	6.9	2.3	5.5	25	26	25	19	2.4	2.9	2.0
C–C–C	3.1	3.2	0.3	0.7	5.1	5.3	4.9	3.0	26	25	18
	1.0	0.9	0.1	0.3	0.2	0.3	0.2	2.0	1.0	1.7	1.6
C–C–C–C	1.1	1.2	0.2	—	3.6	4.2	2.2	—	1.1	1.0	—
C_5	0.4	0.3	0.3	—	1.0	1.1	0.3	0.7	2.5	2.3	0.6
C_6	1.1	1.3	—	—	—	—	—	—	—	—	—
C_6	1.2	1.1	0.3	—	1.2	1.4	0.3	—	2.0	1.4	—
C_7	1.0	1.1	—	—	0.5	0.5	0.2	—	0.3	0.0	—
C_8	—	0.7	—		0.6	0.8	—	—	0.3	—	—

one-third its former value. Similar changes were observed by El-Sayed and Wolfgang[3] when the intensity of the neutron flux was varied by a factor of 2000. With ethane and propane, however, there is no such sharp difference between experiments A and C, apparently because while the radiolysis of methane produces mainly CH_3 radicals and H atoms, which react with thermal tritium atoms to give labelled hydrogen and labelled methane, and increasing the radiation dose increases the number of these radicals and so the total yield of labelled methane and hydrogen, the radiolysis of ethane and propane produces, in addition to the radical of the parent molecule and a hydrogen atom, considerable amounts of methyl and ethyl radicals, which give final products other than labelled parent compound and hydrogen. Increase of the radiation dosage will cause thermal tritium atoms to react with these radicals also, so increasing the yield of methane in the irradiation of ethane, and of methane and ethane in the irradiation of propane. This assumption finds ready confirmation in the data of Table 10. It is interesting to note that irradiation of methane, ethane, and propane for 3 min in a flux of 2×10^{12} neutrons cm^{-2} sec^{-1} gives a higher yield of labelled hydrogen than irradiation for 1 h in the same flux; this is apparently because in the short time of 3 min the system does not have time to attain a state of equilibrium, *i.e.* the concentration of radicals has not reached a stationary value. In such a case the thermal tritium atoms will react mainly with the parent compound with the abstraction of a hydrogen atom and the formation of labelled hydrogen.

When lithium salts are used to obtain the recoil tritium atoms the dosage from the recoil atoms is considerably reduced by taking particles of the salt of a certain diameter. The free path of recoil tritium atoms of initial energy 2.7 MeV is much greater than the average size of the particles of a finely ground salt. By choosing large salt particles a large fraction of the free path of the recoil atoms will lie within the particles. The free path of α-particles is 20% less than that of the recoil tritium atoms, so that the diameter of the particles can be so chosen that all the α-particles remain in the crystal, while the tritons leave it with reduced energy. It has been shown experimentally that for a given specific activity the life of the irradiated compound is greater when using coarse particles than with the salt as a fine powder. For example, the irradiation of cholesterol mixed with 60 μ particles of lithium oxalate gave a good yield of a substance having a specific activity of 200 μc g^{-1}; the same amount of irradiation using 30 μ particles gave greater decomposition, and the use of a lithium myristate gel caused the formation of an insoluble product from which no cholesterol could be isolated[39].

The stability of various compounds to irradiation is given in Table 11; it decreases with increasing molecular weight of the irradiated compound.

TABLE 11. Stability of some organic compounds towards radiation.

Substance irradiated	Mol. wt.	Li salt in irradiated mixture, %	Flux, 10^{12} neutrons per cm^2 per sec	Period of irradiation	Introduction of tritium into irradiated compound, %	Survival of irradiated compound, %	Ref.
Methane	16	90	5	30 sec	47	100	11
Ethane	30	90	5	30 sec	41	100	11
Ethanol	46	12	2	6 h	23	95	19
Benzene	78	50	4	100 h	26	60	16
Cyclohexa-1,4-diene	80	50	4	10 h	17	30	17
Cyclohexa-1,3-diene	82	50	4	10 h	11	75	17
Benzoic acid	122	17	2	40 h	—	35	7
Ditto		5	2	154 h	—	66	7
»		1	2	700 h	—	56	7
Nicotinic acid		10	2	48 h	6	$\sim$ 50	7
Phenylacetic acid	136	3	2	3 h	31	$\geqslant$ 95	7
Glucose	180	50	0.006	72 h	10	$\geqslant$ 95	21
Galactose	180	10	2	27 h	12	$\geqslant$ 32	21
Phenyltriphenoxysilane	393	1	10	12 h	24	$\geqslant$ 76	53
Tetraphenoxysilane	411	1	10	12 h	23	73	53
Reserpine	608	10	2	2 h	18	6	7

4. THE ISOTOPE EFFECT OF RECOIL TRITIUM ATOMS

When recoil tritium atoms were reacted with partially deuterated methane molecules, the activity (calculated per atom of hydrogen or deuterium) was greater for HT than for DT[36] (Table 12). For CH_2D_2 the ratio HT/DT is 1.4, which is in good agreement with the ratio of the vibrational frequencies for C–H and C–D bonds. The ratio HT/DT = = 1.27 obtained for a mixture of CH_4 and CD_4 is a combination of the relative probability of reaction of a recoil atom with each molecule and the probability of the abstraction of hydrogen from the parent molecule. The ratio HT/DT = 1.6 for a mixture of H_2 and D_2 also includes these two probabilities, and also a factor due to the large difference in the velocities of the centres of mass in the reaction of H_2 and D_2 with a tritium atom of the given velocity[33].

TABLE 12. Reactions of recoil tritium atoms with deuterated methane and deuterium; irradiation for 48 h in a flux of 3×10^9 neutrons per cm^2 per sec.

	Pressure, mm Hg				HT/DT	HT/DT $\frac{CH_4}{CD_4}$	HT+DT $\frac{CH_3T+CHD_2T}{}$	HT/DT $\frac{H_2}{D_2}$
CH_2—D_2	CH_2D_2		^3He	NO	1.34+0.02		0.84	
	746		29	—	1.40+0.02	—	0.83	
	260		29	—			0.83	
	102		29	—	1.42+0.02	—	0.90	
	747		14	56	1.19+0.07	—	0.82	
CH_4—CD_4	CH_4	CD_4	^3He	NO			HT+DT $\frac{CH_3T+CD_3T}{}$	
	338	398	14	—	1.09	1.29	0.82	
	552	181	14	—	3.83	1.26	0.82	
	374	374	11	56	1.28	1.28	0.80	
H_2—D_2	H_2	D_2	^3He	NO				
	396	310	17	—	1.97	—	—	1.55
	612	90	17	—	9.93	—	—	1.45
	120	581	17	—	0.35	—	—	1.68
	304	321	10	4.3	2.65	—	—	2.79

In the reaction of recoil tritium atoms with isopropyl benzoate it was found[23] that the isotope effect H/D is 1.41 for aliphatic hydrogen atoms and 1.16 for aromatic. The introduction of tritium into benzene[16] gave an isotope effect of 1.14.

The difference in the isotope effects for aliphatic and aromatic hydrogen atoms may be because in the latter case the tritium is initially captured by the aromatic bonds and this is followed by elimination of a hydrogen atom, while in aliphatic hydrocarbons there is first a weakening of the C–H bond and then replacement of hydrogen by tritium.

5. THE INTRAMOLECULAR DISTRIBUTION OF RECOIL TRITIUM ATOMS IN THE LABELLED PRODUCTS

Normally a labelled compound obtained by reaction with a recoil tritium atom is active in all hydrogen positions, but the relative tritium content in different positions varies greatly in many cases; for instance, the labelled benzoic acid obtained from *o*-hydroxybenzoic acid has 87% of the total activity of the molecule in the *ortho*-position, while the activity in the *para*-position is almost zero (Table 13).

In the general case the distribution of tritium within the parent molecules tends to an equal probability distribution. The intramolecular distribution will deviate from equal probability mainly because of steric factors; for example, the different tritium distributions in *cis*- and *trans*-cinnamic acids is because the COOH group in the former effectively screens one of the *ortho*-positions, and the tritium distribution in the *cis*-acid is approximately as if one of the *ortho*-positions has no tritium at all[25].

In cyclohexene the hydrogen at the double bond is more easily replaced by a recoil tritium atom than hydrogen at a saturated carbon atom; however, no such difference was observed with cyclohexa-1,3-diene[41].

The specific activities for individual hydrogen positions differ particularly greatly in molecules obtained as the result of decomposition of the parent molecule. It has been

TABLE 13. Intramolecular tritium distribution in the reaction products of hot tritium atoms.

Substance	Activity in the given position, %	Activity per hydrogen atom, %	Ref.
Ethanol	36 26 38	12 13	17
Cyclohexanol	60 40	5.4 40	17
Isopropyl benzoate	64 6 30	13 6 5	23
Toluene	*o* 34.0 *m* 28.0 *p* 16.0 22.0	17.0 14.0 16.0 7.3	18,40
Glucose	3 (3) 6 (6) 29 (50) 14 (2) 0 (23) 48 (16)	3 6 29 14 0 24	21(22)
Galactose	8 5 22 32 11 22	8 5 22 32 11 11	22
Benzoic acid obtained from:			
o-$NH_2C_6H_4COOH$	*p* 1 *m* 7 *o* 92	1 3.5 46	26
m-$NH_2C_6H_4COOH$	*p* 7 *m* 86 *o* 7	7 43 3.5	26
p-$NH_2C_6H_4COOH$	*p* 88 *m* 12 *o* 0	88 6 0	26
o-$NO_2C_6H_4COOH$	*p* 8 *m* 10 *o* 82	8 5 41	26
m-$NO_2C_6H_4COOH$	*p* 7 *m* 80 *o* 13	7 40 6.5	26
p-$NO_2C_6H_4COOH$	*p* 78 *m* 19 *o* 3	78 9.5 3	26

TABLE 13 (contd).

Substance	Activity in the given position, %	Activity per hydrogen atom, %	Ref.
o-HOC_6H_4COOH	*p* 0 *m* 13 *o* 87	0 6.5 43.5	26
m-HOC_6H_4COOH	*p* 8 *m* 82 *o* 10	8 41 5	26
p-HOC_6H_4COOH	*p* 77 *m* 12 *o* 11	77 6 5 5	26
o-BrC_6H_4COOH	*p* 4 *m* 7 *o* 89	4 3.5 44.5	26
m-BrC_6H_4COOH	*p* 7 *m* 84 *o* 9	7 42 4.5	26
p-BrC_6H_4COOH	*p* 72 *m* 22 *o* 6	72 11 3	26
o-IC_6H_4COOH	*p* 8 *m* 9 *o* 84	7 4.5 42	26
m-IC_6H_4COOH	*p* 12 *m* 86 *o* 2	12 43 1	26
o-FC_6H_4COOH	*p* — *m* — *o* 64	— — 32	26
m-FC_6H_4COOH	*p* — *m* 82 *o* —	41 — —	26
o-ClC_6H_4COOH	*p* — *m* — *o* 86	— — 43	26
p-ClC_6H_4COOH	*p* 72 *m* — *o* —	72 — —	26
o-$C_6H_4(COOH)_2$	*p* 7 *m* 24 *o* 69	7 12 34.5	26
Aniline obtained from:			
o-$NH_2C_6H_4COOH$	*p*, *m* 4 ±4 *o* 96±4	4 —	26
m-$NH_2C_6H_4COOH$	*p*, *m* 12±1 *o* 88±1	12 —	26
p-$NH_2C_6H_4COOH$	*p*, *m* 75±1 *o* 25±1	75 —	26
Phenylacetic acid	*p* 18.3 *m* 29.0 *o* 29.0 1.6	18.3 14.5 14.5	28
Benzoic acid	*p* 21 *m* 36 *o* 43	21 18 21.5	25
Benzoic acid	2.2 94 7.2	2.2 47 3.6	43
cis-Cinnamic acid	*p* 23.5 *m* 42 *o* 22.5 β, α 12	23.5 21 11,25 —	25
trans-Cinnamic acid	*p* 16.8 *m* 30.8 *o* 33.4 β 11.5 α 7.6	16.8 15.4 16.7 11.5 7.6	25
trans-Cinnamic acid Na salt	*p* 16.8 *m* 30.8 *o* 33.4 β 11.5 α 7.6	16.8 15.4 16.7 11.5 7.6	25
L(+)-Alanine(solid)	β 80 α 20	27.0 20	20
L(+)-Alanine(aq. soln.)	β 100 α 0	33.3 0	20
D(−)-Alanine obtained from *L*(+)-alanine	β 100 α 0	33.3 0	20
D(−)-Alanine obtained from *L*(+)-alanine(aq. soln.)	β 86.5 α 14.5		20
Cyclohexene	at the C=C bond 24.4 at the C—C bonds 75.6	12.2 9.5	41
Cyclohexene obtained from cyclohexa-1,3-diene	at the C=C bond 13.6 at the C—C bonds 86.4	6.8 10.8	41
Cyclohexa-1,3-diene	at the C=C bond 28.5 at the C—C bonds 75	12.5 12.1	41

shown[26] that in labelled benzoic acid obtained from substituted benzoic acids 70–90% of the tritium occupies the position of the original substituent atom or radical, and as a rule the activity in other positions decreases as the distance from this position increases. A compound labelled in a particular position can be obtained in this way.

With $L(+)$-alanine the intramolecular tritium distribution depends on the irradiation conditions[20]. Alanine irradiated as crystals has 82 ± 2% of the tritium in the β-position and 18 ± 2% in the α-position, while when irradiated in aqueous solution it has 98 ± 2% and 2 ± 2% of the total activity in these positions respectively.

Variation of the period of irradiation and the intensity of the neutron flux by a factor of ten has no noticeable effect on the distribution of tritium in benzoic acid obtained from substituted benzoic acids.

Comparison of the intramolecular tritium distribution in toluene, benzoic acid, and *trans*-cinnamic acid demonstrates that the substituents have little influence on the distribution of tritium within the aromatic ring.

It should be noted that Okamoto[43] obtained results on the intramolecular distribution of tritium in benzoic acid which were completely different from those obtained by Milford and Rowland[25].

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The characterisitics which have been described for the reaction of recoil atoms and ions with a substance make it possible to choose the best method for the synthesis of labelled compounds. The choice of the initial mixture to be irradiated, the irradiation conditions, and the subsequent treatment to isolate the labelled products is dictated not only by the product which must be obtained, but also by the mechanism by which the product is obtained from the initial substance. Each mixture to be irradiated and each product desired requires individual choice of materials to be added, the method of irradiation, the isolation of the product, and so on. However, the following general considerations can be applied with benefit in choosing the conditions for the hot synthesis of labelled compounds.

1. The reaction products of hot atoms contain the labelled parent molecule, but the specific activity of the latter cannot be high, since because of radiolysis the optimum period of irradiation is 100–200 h for reaction with recoil carbon-14 atoms, and 10–20 h for tritium.

A considerable fraction of the labelled compounds is made up of products obtained by substitution of carbon-14 or tritium for atoms or radicals such as nitrogen, halogens, and the C_2H_5 group. These products are obtained with high specific activity.

Hydrogenation of unsaturated compounds and dehydrogenation reactions are also characteristic of reactions with tritium. The most probable reaction is the replacement of atoms of similar mass, carbon and nitrogen for carbon, and hydrogen for tritium. In many cases the substitution is accompanied by molecular rearrangement.

A considerable fraction of radioactive atoms forms high-boiling products, polymers, particularly in the case of reaction products obtained from recoil ^{14}C atoms. Products of decomposition of the molecule, *i.e.* the gaseous fraction, play a particularly large part in the case of tritium

2. If the molecule of the initial substance takes part directly in the reaction with a hot atom, the substance must be stable to radiation, and the irradiation conditions must reduce radiation effects to a minimum.

3. If the desired labelled product is the product of reaction of a hot atom with fragments of the initial molecules produced by radiolysis, the initial substance should give the maximum number of such fragments on irradiation. The irradiation conditions will also be chosen with this mechanism of product formation in mind.

4. If the product is formed by hot reactions, the phase state of the system is unimportant; however, if the product is expected to be formed by a superthermal reaction, it is best to irradiate solid samples. For maximum yield of products of thermal reactions the irradiation is best conducted in the liquid or gaseous phase.

5. In all cases the irradiation must be effected at temperatures at which the substance is thermally stable; the temperature has no influence on the yield of products from hot reactions, but does influence the yield from thermal reactions, since altering the temperature affects the lability and life-time of individual radicals. Subsequent heating of the mixture may also be useful in increasing the yield of labelled products from thermal reactions.

6. All additives dilute the irradiated substance. To decrease the dilution effect when additives are added (*e.g.* nitrogen-containing substances in the irradiation of hydrocarbons) they may be used in an insoluble form, *i.e.* heterogeneous systems may be employed.

7. The specific action of additives is dictated by the mechanism of formation of the labelled substance. Thus the dilution effect is the main influence on the yield of hot reactions, while the addition of radical acceptors considerably reduces the yield of labelled compounds obtained by superthermal reactions.

8. Addition of substances which can become excited reduces the decomposition, by the radiation, of the initial materials and the products of their reactions with hot atoms, and so increases the yield of such products.

9. Additives which undergo normal chemical reaction with the labelled products decrease the yield of the latter, because of secondary thermal reactions.

10. Substances which under the irradiation conditions produce fragments able to take part in the formation of the required labelled compounds should presumable increase their yield.

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HYDROXIDE CHLORIDES AND HYDROXIDES OF ELEMENTS OF THE SCANDIUM SUBGROUP AND OF THE LANTHANIDES

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