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The Reactions of Recoil Tritium with Gaseous Hydrocarbons[1]

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Recoil tritium reactions with *trans*-butene-2, *cis*-butene-2, isobutylene, propylene and propane have been investigated under a variety of experimental conditions. The yields of certain "hot" products, *e.g.*, propylene from butene-2, depend upon the gas pressure during irradiation, because of the variation in mean time before collisional deactivation of excited *sec*-butyl radicals produced in the original "hot" reactions. The high kinetic energy of recoil tritium atoms enables them to react almost equally well with saturated and unsaturated positions, both in intermolecular and intramolecular competition, by making differences in activation energy for reaction of minor importance. A general hypothesis for recoil tritium reactions at saturated and unsaturated carbon atoms is presented.

Introduction

Tritium atoms recoiling from the nuclear reactions Li^6(n, α)T and He^3(n, p)T undergo reactions with essentially all organic molecules, with the introduction of 10 to 50% of the radioactivity into the otherwise unchanged parent molecule.[2] In a few systems, the chemical identity of the rest of the tritium has been reported: a substantial fraction (30–75%) appears as HT, and the balance in close relatives of the parent compound.[3-10]

It has seemed to us that the understanding of these recoil reactions would be greatly aided by measurement of the yields of all important labeled products from the tritium reactions with a series of related molecules, such as the hydrocarbon gases. Irradiations of gaseous mixtures of hydrocarbons and He^3 already have been reported for methane,[5-8] ethane,[7,8] propane[5] and butene-1.[8] Urch and Wolfgang recently have published a preliminary report on a number of unsaturated molecules.[10] In the course of the various experiments, the observed pattern of labeled products has been shown to be strongly dependent on the presence of other gases, such as I_2 and Br_2, which can function as radical scavengers, and helium, which acts as a moderator in reducing the energy of the recoiling tritium atom.

We have investigated the products of the tritium recoil reaction in gas mixtures of He^3 and organic hydrocarbons in the range C_1–C_4. In addition, we have tested the influence of other gases on these reactions in particular systems, using nitric oxide or helium.

Experimental

Gases.—The hydrocarbons were all obtained from the Matheson Company, with quoted purity > 99%. A number of samples have been purified to > 99.99%, with no apparent effect on the results. In all samples, radiation damage produces measurable quantities of impurities during the irradiation, so that extreme purificaton is not worth-while. The moderator and scavenger gases were also taken directly from lecture bottles or tanks, all with quoted purity of >99%, or better. He^3 was obtained from Oak Ridge; the radioactive impurities (T_2, HT and saturated hydrocarbons through C_5) were removed by combustion over CuO at 600° and passage through a liquid nitrogen trap.[11]

Irradiations.—The gas samples were sealed in a vacuum system into Pyrex 1720 glass bulbs equipped with breakseals. Originally, the bulbs were of 8 mm. i.d. tubing and 5–10 cm. long. Later, all bulbs have been made of 20 mm. i.d. tubing to increase the total sample size and permit reduction of irradiation times. The irradiations were carried out under a variety of experimental conditions in the CP-5 Argonne reactor and the Brookhaven reactor. Neutron fluxes ranging from 2×10^9 to 5×10^{12} n./cm.^{2}/sec. have been used.

After irradiation, the bulbs were opened in a sampling device equipped with a Toepler pump. As much as 80% of the gaseous sample was used in the first aliquot; smaller aliquots were used on additional runs.

Observed Tritium Yields.—The He^3(n,p)T reaction produces tritium ions with a recoil energy of 192,000 e.v., which corresponds to a range of approximately 2.4 mm. in CH_4 at 15° and 76 cm. pressure.[12] Since this recoil range is not always small compared to the diameter of the irradiation bulbs, an appreciable fraction of the total tritium activity produced can strike the walls before reaching thermal energies. Since the recoil range is much longer in He and much shorter in C_4 hydrocarbons at the same pressure, the fraction lost into the walls will vary substantially depending on the composition of the gas mixture. This loss cannot be calculated exactly because of incomplete knowledge of the pertinent stopping powers in this energy region but in some cases exceeded 95% with small bulbs. In the larger bulbs, the percentage recoil loss is greatly reduced and may be neglected except for low pressure irradiations.

A further experimental hazard is presented by the presence of the T atoms whose recoil energy imbedded them into the wall. Other experimenters[7] have found that quartz bulbs permit the diffusion of these T atoms back into the gas space again, resulting in an increase in observed HT, but not of labeled hydrocarbons. Pyrex 1720, a high-melting aluminosilicate glass (plus 5% B_2O_3 and 0.5% Na_2O), has been shown, in contrast to quartz, not to be permeable to HT diffusion at 650°.[13] Subsequent heating of some of our used 1720 Pyrex bulbs for an hour at 110° showed no measurable T activity reappearing in the gas phase, eliminating any necessity for a "diffusion" correction in these experiments. The high B and Na contents, however, are somewhat inconvenient because of the neutron absorption and resultant radioactivity, respectively.

Gas Chromatographic Analysis.—The various labeled products were separated by gas-liquid partition or gas adsorption chromatography, the radioactivity measured by

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(1) Research supported by A. E. C. Contract No. AT-(11-1)-407. Presented in part at the 134th Meeting of the American Chemical Society, Chicago, September, 1958.

(2) For example, see the list in F. S. Rowland and R. Wolfgang, *Nucleonics*, **14**, No. 8, 58 (1956).

(3) R. Wolfgang, J. Eigner and F. S. Rowland, *J. Phys. Chem.*, **60**, 1137 (1956).

(4) W. J. Hoff, Jr., and F. S. Rowland, THIS JOURNAL, **79**, 4867 (1957).

(5) A. A. Gordus, M. C. Sauer and J. E. Willard, *ibid.*, **79**, 3284 (1957).

(6) M. El-Sayed and R. Wolfgang, *ibid.*, **79**, 3286 (1957).

(7) M. El-Sayed, P. Estrup and R. Wolfgang, *J. Phys. Chem.*, **62**, 1356 (1958).

(8) R. Wolfgang, with F. S. Rowland, M. El-Sayed, P. Estrup, C. McKay and D. Urch, Second United Nations International Conference on the Peaceful Uses of Atomic Energy, Geneva, 1958, United Nations Publications, **29**, 326 (1959).

(9) R. Milford White and F. S. Rowland, 135th Meeting of American Chemical Society, Boston, April, 1959.

(10) D. Urch and R. Wolfgang, THIS JOURNAL, **81**, 2025 (1959).

(11) J. K. Lee and F. S. Rowland, *J. Inorg. & Nuclear Chem.*, **10**, 336 (1959).

(12) C. Cook, E. Jones and T. Jorgensen, *Phys. Rev.*, **91**, 1417 (1953).

(13) K. Wilzbach, L. Kaplan and W. G. Brown, Argonne National Laboratory Report, ANL-5056 (1953).

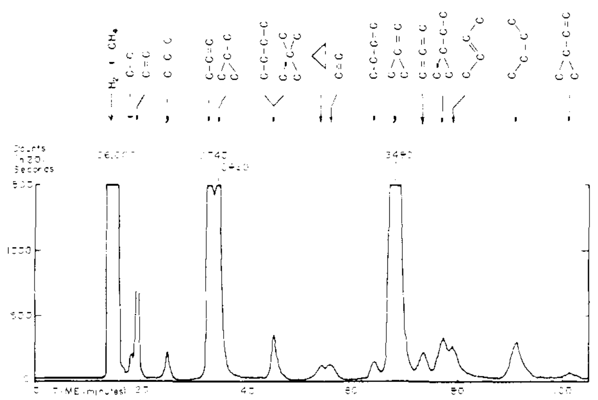

Fig. 1.—Distribution of tritium activity following tritium recoil reaction in gas phase; 31.1 cm. $\underset{C}{\overset{C}{>}}C{=}C$; 1.9 cm. He^3; 50′ dimethylsulfolane, 25°, 25 ml./min.

passage through a proportional counter and the molecule identified by the characteristic retention time. The proportional counting apparatus was similar to that recently described[14]: methane was added to the flowing gas stream (and labeled products) after separation but prior to flowing through a silver-walled proportional counter of 20 ml. active volume.[15]

Several aliquots of each sample were measured, each with a different column packing. The most useful separations (see Fig. 1) were those obtained on a 50′ column made of $^1/_4$″ o.d. copper tubing and packed with dimethylsulfolane (abbreviated DMS) adsorbed on 30–60 mesh fire brick,[16] operated at 20 lb. pressure of helium and a flow rate of 25 ml./min. at 25°.[17]

These mass peaks were all similarly shaped and had a full width at half-maximum of about 3% of the measured retention time. When larger bulbs were used, the parent peak was distorted by the overloading of the column, but the minor peaks maintained their shape and approximate retention volume.

The dimethylsulfolane column produces clean separations of more than 20 peaks of C_5 or less, most of which represent single compounds. The most important unresolved pairs in this separation are ($H_2 + CH_4$) and (C–C–C–C + $\underset{C}{\overset{C}{>}}C\underset{C}{\overset{C}{<}}$).

Four other pairs of peaks are closely spaced enough to make measurement of the second component (C=C, $\underset{C}{\overset{C}{>}}C{-}C$, C≡C and $\overset{C\quad C}{\diagdown C{=}\diagup\ \diagdown C}$) difficult in the presence of very large amounts of the first component. The sharp front edge of the peaks makes interference of the second with the first much less important. After about C_5, the identification of peaks is less certain because of the large number of uncalibrated hydrocarbons.

A second aliquot was run on a 6′ column packed with silica gel, which provided clean separations and measurement of H_2, CH_4, C—C, C=C, C–C–C and C≡C (140 ml./min., 25°, 10 lb. He).

Aliquots were also run on an 8′ Narcoil column (Burrell Co.) primarily as a check on reproducibility and consistency (75 ml./min., 25°, 15 lb. He). Since saturated and unsaturated molecules of equal carbon number come out rather close to one another on the Narcoil column, this aliquot served as a check against substantial yields of samples not measured on dimethylsulfolane (*e.g.*, C–C–C≡C, C–C≡C–C etc.). In some recent runs, the Narcoil column has been replaced with either a 50′ or 20′ column packed with safrole on fire-brick in order to separate *n*-butane from neopentane and 2,3-dimethylbutane from isohexane, respectively, in convenient time periods.

As the flow rate of CH_4 + He through the proportional counter was 50 ml./min., the average molecule separated on the dimethylsulfolane column spent about 24 seconds in the active counting volume of the counter. This time spread in detection of a peak broadened the radioactivity peak of $H_2 + CH_4$, and other early compounds to some extent, relative to the calibrated mass peaks. It did not interfere with the resolution of any peaks, however, as in Fig 1. The higher flow rates used through the silica gel and Narcoil columns avoided any appreciable broadening of the radioactivity peaks relative to the mass peaks.

None of the chromatographic columns were programmed for temperature rise because of the necessity of maintaining a constant flow of gas through the proportional counter. The threshold and dead-time of the counter are sensitive to changes in the CH_4–He ratio, and the measurements of relative radioactivity assume a flow rate independent of time. A further limitation of the present system is the necessity for operating the counter at about 25°.

No important discrepancies appeared in the measurements of individual compounds, as indicated on different columns, with the exception of the first three high-activity aliquots (peak ≅ 3000–4000 counts/sec.) run on the dimethylsulfolane column. These showed less activity in the ($H_2 + CH_4$) peak than indicated by the corresponding Narcoil aliquot, because of appreciable coincidence loss at high count rates. Adjustment of CH_4 flow rate and voltage setting eliminated this difficulty in all subsequent samples. The present arrangement has less than 3% coincidence loss at 6000 counts/sec. Separate calibration experiments have demonstrated that the counting efficiency of the counter is not affected by the gases other than CH_4–He in the amounts used here.

Results

The distributions of observed tritium activity among HT and various hydrocarbons are shown in Tables I–V. The activities are given relative to the parent molecule = 100, except in Table V, in which percentages of total observed activity are used. For most runs, the accuracy of analysis of a particular sample is good to ±1 or 2%, standard deviation, for the important peaks. The significance of the minor peaks is reduced by the radiation damage occurring during irradiation. Even peaks containing as much as 1% of the total radioactivity may be distorted by radiation damage in our best runs; for this reason, although we have observed very low yields for many products, only those with yields ≥1% of the parent molecule are included in Tables I–IV. All of the observed products are listed for three runs in Table V.

Our usual chromatographic analysis does not show any hydrocarbon peaks in the region of C_7 or higher, nor would it show any but the lowest molecular weight non-hydrocarbons. In some cases, we have specifically looked for higher molecular weight hydrocarbons and found them to be present but unimportant in percentage of total activity. No appreciable tritium activity is missing from the runs listed in the tables, and we do not feel that unobserved higher molecular weight products would alter the conclusions.

The identification of particular products has been made solely on the basis of retention time of calibration mass peaks on the various columns. The absence of radioactivity peaks except in coincidence with known hydrocarbons, and the agreement from column to column, makes it very unlikely that any of the observed peaks are actually molecules other than the indicated hydrocarbon,

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[14] R. Wolfgang and F. S. Rowland, *Anal. Chem.*, **30**, 903 (1958).

[15] Roman Scientific Glass Co., 57 Everett St., Patchogue, New York.

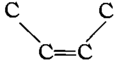
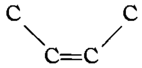
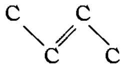
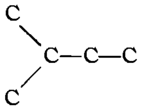
[16] E. M. Fredericks and F. R. Brooks, *Anal. Chem.*, **28**, 297 (1956).

[17] Except for HT and CH_3T, all compounds are identified in the ables by the appropriate carbon skeleton.

TABLE I

RADIOACTIVE PRODUCTS FROM $He^3(n,p)T$ REACTION WITH *cis*-BUTENE-2

(Observed activity relative to *cis*-butene-2 equals 100)

Press, cm. 	58.3[a]	55.6	49.2	64.0	64.0	34.7	[b]
He^3	1.0	1.0	1.2	1.4	1.4	1.7	
Time	5 min.	5 min.	10 min.	40 hr.	40 hr.	48 hr.	
Flux	5×10^{12}	5×10^{12}	5×10^{12}	2×10^9	2×10^9	2×10^9	
	100	100	100	100	100	100	100
C—C—C=C	16	17	17	15	15	16	14
	11	11	11	9	10	10	13
C—C=C	80	79	80	81	77	89	69
C=C	5	5	6	5	5	5	5
HT	195	200	191	208	209	222	191
CH_3T	11		12	11			15
C—C	1	1	1	1	1	1	1
C—C—C—C	25	25	25	30	28	36	58
	8	11	11	7	7	10	..
C≡C	2	2	2	2	2	2	..
C=C=C	1	1	1	1	1	1	..
C=C—C=C	2	1	2	2	1	1	..

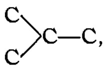
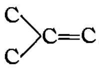
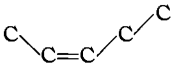
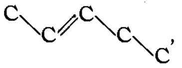
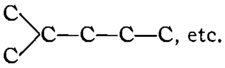
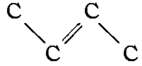
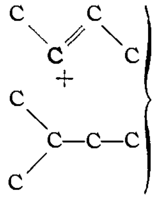
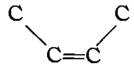
[a] Other products from this run: C—C—C, 0.2; C—C≡C, 0.5;  , <0.2;  , <0.2. Traces (~<0.5) of  ,  ,  , etc. [b] Urch and Wolfgang, ref. 10.

TABLE II

RADIOACTIVE PRODUCTS FROM $He^3(n,p)T$ REACTION WITH *trans*-BUTENE-2; EFFECT OF PRESSURE

(Observed activity relative to *trans*-butene-2 equals 100)

Pressure, cm. 	69.4	72.8	63.9	24.3	9.6	[a]
He^3	1.5	1.5	1.6	1.5	1.5	
Time	5 min.	48 hr.	40 hr.	48 hr.	48 hr.	
Flux	5×10^{12}	2×10^9	2×10^9	2×10^9	2×10^9	
	100	100	100	100	100	100 ..
C—C—C=C	14	13	15	16	16	12
	5	5	6	7	9	13
C—C=C	61	58	58	66	73	60
C=C	4	4	4	5	5	4
HT	179	180	173	168	172	171
CH_3T				7	8	11
C—C	1	1	1	1	1	1
C—C—C—C	23	30	25	22	21	46
C≡C	2	2	2	2	2	..
C=C=C	1	1	1	1	1	..
C—C≡C	1	1	1	1	1	..
C=C—C=C	1	1	1	1	1	..

[a] Urch and Wolfgang, ref. 10.

even in samples containing nitric oxide. Although it is known that the labeled compounds may show observable differences from the unlabeled molecules in retention times, it should not be important here. The tritium concentrations are so low that doubly T-labeled molecules are completely negli-

TABLE III

RADIOACTIVE PRODUCTS FROM $He^3(n,p)T$ REACTION WITH *trans*-BUTENE-2; SCAVENGER, MODERATOR EFFECTS

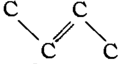
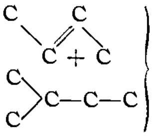
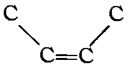
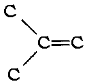
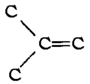
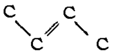
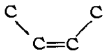
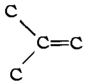
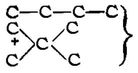
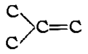
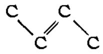
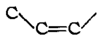
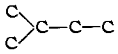
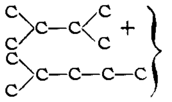
Pressure, cm.					
	67.8	23.6	9.9	22.8	9.8
He^3	1.2	1.6	1.6	1.5	1.7
Other	7.3 NO	2.5 NO	2.7 NO	51.8 He^4	65.9 He^4
Time, flux		All irradiated for 48 hr. at 2 × 10^9 n./cm.^{2}/sec.			
	100	100	100	100	100
C—C—C=C	32	48	53	21	12
	7	14	17	8	8
C—C=C	57	66	76	59	69
C=C	4	4	3	5	5
HT	169	167	190	181	224
CH_3T	6	7	9	8	7
C—C	0	0	0	10	3
C—C—C—C	0	0	0	45	34
C≡C	2	2	2	2	2
C=C=C	0	1	1	0	1
C—C≡C	1	1	1	1	2
C=C—C=C	1	1	1	1	3

TABLE IV

RADIOACTIVE PRODUCTS FROM $He^3(n,p)T$ REACTION WITH VARIOUS HYDROCARBONS; LONG IRRADIATIONS

			C—C=C	C—C=C	C—C—C				C—C=C[b]	C—C—C
Pressure, cm.										
Parent	53.4	31.7	52.1	10.9	52.0	31.5	31.7	31.1	31.2	30.0
He^3	2.0	1.3	1.2	1.3	1.3	1.9	1.7	2.3	1.9	2.5
Time	48 hr.	48 hr.	40 hr.	6 days	5 min.	All 12 hr. at 1 × 10^{12}				
Flux	2 × 10^9	2 × 10^9	2 × 10^9	3 × 10^9	5 × 10^{12}					
HT	86	95	76	71	287	398	491	344	194	297
CH_3T	5	6	3	3	14	29		32	13	27
C—C	0	0	0	0	9	8	11	2	2	21
C=C	1	0	33	33	6	22	28	8	42	2
C≡C	0	1	1	3	1	7	10	3	6	1
C—C—C	0	0	11	9	100	7	9	2	18	100
C—C=C	21	21	100	100	2	101	99	44	100	2
C=C=C	1	2	1	1	0	3	3	4	2	0
C—C≡C	..	2	1	1	0	4	..	4	..	..
	0	1	1	1	3	70	72	7	3	7
C—C—C=C	..	.	1	1	0	23	26	4	2	0
	100	100	0	0	0	2	1	100	2	1
	0	0	0	0	0	100	23	6	1	0
	0	0	0	0	0	54	100	8	1	0
C—C—C—C—C	0	0	0	0	1	1	1	0	1	2
	1	2	1	1	6	9	10	8	2	10
			15	10	4					8
C—C—C—C—C—C				6	0					..

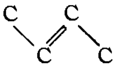
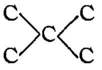
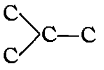
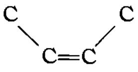
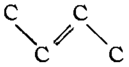
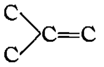
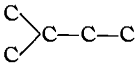
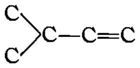
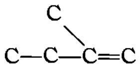
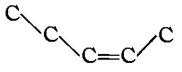
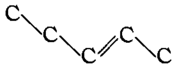
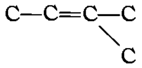
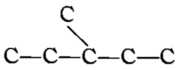
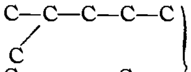
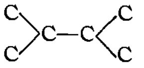
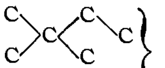
[a] Also, cyclopropane, 3. [b] Also, cyclopropane and methylcyclopropane, each 1.

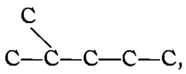
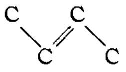
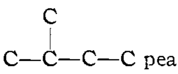
gible—the effect on singly-labeled molecules should be comparatively small, and would further tend to cancel since all of the radioactive molecules would be affected by the presence of one tritium atom.

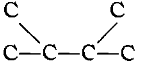
Radiation Damage.—One of the most difficult experimental problems in these systems is the elimination or control of macroscopic radiation damage effects. The importance of such reactions can be seen by comparing the results for widely different total neutron exposures in different irradiations. Mass peaks were recorded on all of these samples by thermal conductivity measurements, although with much poorer sensitivity than for the radioactive peaks. Compounds other than the parent molecule, not present at the beginning of the irradiation, always were observed. In the runs with larger bulbs and lower total neutron exposures, these macroscopic radiation damage peaks were correspondingly reduced. Table VI shows the observed impurities introduced by radiation

TABLE V

RADIOACTIVE PRODUCTS OF THE RECOIL TRITIUM REACTION IN PROPANE-*trans*-BUTENE-2 MIXTURE[a]

Pressure, cm.		62.2	25.8	0
	C—C—C	0	50.3	45.2
	He^3	1.5	1.7	1.3
Irradiation	Time	40 hr.	48 hr.	10 min.
	Flux	1×10^9	3×10^9	5×10^{12}
Product				
HT		42.19	42.41	63.20
CH_3T		2.41	3.48	3.03
C—C		0.10	1.37	2.29
C=C		0.98	2.07	1.12
C≡C		0.38	0.21	0.12
C—C—C		0.04	18.26	23.60
C—C=C		14.98	7.11	0.38
C—C≡C		0.10	0.07	0.02
C=C=C		0.17	...	...
Δ		A	A	A
 C—C—C—C		6.34	7.13	0.82
		...	...	1.97
C—C—C=C		4.47	3.39	0.04
		1.65	0.78	...
		25.82	12.68	D
		...	...	0.05
C—C—C—C—C		...	...	0.35
		C	C	1.59
C—C—C—C=C		...	...	...
		0.08	0.12	...
		...	...	B
		...	0.08	...
		B	B	B
		...	...	0.06
C—C—C—C—C—C		...	0.14	0.02
		...	0.57	0.04
 		0.06	0.15	1.26
Δ—C		C	C	...
 C=C—C=C		0.22	0.04	0.05

[a] A, included in C≡C; B, included in  peak; C, included in large  peak; D, included in  peak; ... <0.01%

 peak;

damage in a number of samples of the runs listed in Tables I–V. It is worth noting that all of the observed radiation damage products in the more heavily irradiated sample have specific activities higher than the labeled parent molecule, as shown in the last column of Table VI.

This radiation damage can obscure the actual reactions of the recoil tritium atom with the parent molecule in three ways:

(1) General damage to the system either can alter the chemical identity of labeled molecules after the reaction of T atoms with the parent molecules, or it can introduce impurities into the system so that the recoil T atoms react with some molecular species other than the parent molecule. Both of these effects are greatly reduced by reducing the radiation exposure and hence the general radiation damage in the system.

(2) In high radiation fluxes, many highly reactive ions, radicals, etc., will be produced and will result in a measurable steady state concentration of these potential reactants. These species can compete very well with ordinary thermal reactions and could easily change that part of a product distribution which depended on thermal reactions. The actual perturbation should change very markedly for irradiations at widely different fluxes with the accompanying variations in steady-state concentrations of reactive species.

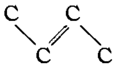
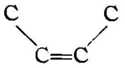
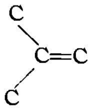
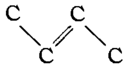
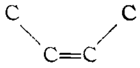
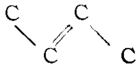
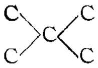
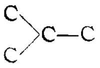
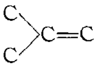
(3) The most important sources of radiation damage in these systems are the energetic triton and proton produced by the neutron reaction with He^3. While the protons contribute to general destruction, each tritium atom will form a stable chemical bond at the end of a long track in which it has dissipated 192 kev. of energy—ionizing about 6000 molecules in the process. These excited species, particularly the last one or two before the stable reaction of the tritium atom, may collide with the labeled products at the end of the track and again alter the distribution. This possibility cannot be removed experimentally since the track will always be formed and can only be measured or alleviated by the introduction of scavenger molecules, pressure changes, etc.

The radiation alterations under (1) and (2) have been essentially eliminated in these experiments, except for the effect on minor components. The lack of widespread radiation damage to the parent molecule implies that, in the absence of extreme radiation sensitivity, the labeled products will not be substantially damaged subsequent to formation, nor will the probability of reaction with a radiation product be important for the original recoiling tritium atoms. (The latter infers roughly equal probability of reaction for the recoil tritium with all molecules. Experimental evidence for this is given below.) The substantial agreement in

Table VI

Hydrocarbon Composition after Irradiation

(Relative Thermal Conductivity Response)

		C—C—C	C—C=C						
Pressure, cm.	Parent	52.0	59.3	64.4	57.9	53.4	44.1		
	He^3	1.1	1.1	1.7	1.1	2.0	1.5		
Irradiation	Time	10 min.	10 min.	10 min.	5 min.	48 hr.	12 hr.		
	Flux[a]	5×10^{12}	5×10^{12}	5×10^{12}	5×10^{12}	2×10^{9}	1×10^{12}		
							Thermal conductivity	Radioactivity	Radio./T.C.
CH_4		4	1	2	2	1	6		
C—C		7		<1	<1	<1	2	12.3	6
C=C		2	<1	3	1	<1	7	45.5	7
C≡C				4	<1	<1	5	22.4	4
C—C—C		>500	54	2	2	5	<1	11.8	>12
C—C=C		3	>600	5	2	<2	9	274	30
C=C=C				<3	<2	<2	<3	6.5	>2
C—C—C=C				4	≤3		8	67.2	8
				25	>10^3	<5	18	43.3	2.4
				>10^3	24	<5	350	418	1.2
C—C—C—C 				6	1	<2	12	133	11
		5		<1	<1	<2			
				<3	<3	>400			

[a] n./cm.^{2}/sec.

experimental results for neutron intensities differing by a factor of 1000 shows that the steady-state radical and/or ion concentration is not a dominant consideration in determining the radioactivity distribution. In those runs carried out for 12 hr. at 10^{12} n./cm.^{2}/sec., macroscopic radiation damage has materially altered the distributions, since about 10–15% of the parent molecules have been decomposed. With saturated hydrocarbons, the observed yields of unsaturated molecules are rapidly suppressed by radiation damage in longer irradiations, as the labeled unsaturates act as scavengers for thermal radicals and hydrogen atoms.

Discussion

The Initial Reaction.—Previous discussions of recoil tritium reactions have explained the observed results on the basis of the reactions of tritium ions or of tritium atoms. These approaches have been adopted largely because of the observed high cross-sections for ion-molecule reactions in the mass-spectrometer,[5] and the preponderance of the neutral state for moving tritium atoms at low energies, respectively.[7] Our interpretation of the results involves neutral T atoms, and not T^+, as the reacting species.

The charge "history" of the recoiling tritium atoms has been discussed in detail by El-Sayed, Estrup and Wolfgang.[7] Although the recoiling tritium is initially a positive ion, it is effectively neutralized by the time it reaches the energy region for chemical bond formation. This region is not clearly defined but probably runs from about 10–100 e.v. down to thermal energies.

Evidence has been presented previously that the reactions of recoiling tritium atoms with organic species are unusual primarily in the possession of substantial excess kinetic energy at the time of reaction. This evidence has been in the form of ease of exchange with methane[6,7] and cyclopropane,[18] both of which have high activation energies for thermal exchange; of observed products indicating enough excess energy to throw off several hydrogen atoms or radicals[4,7]; and especially from the insensitivity of the parent-labeling reaction, as well as other reactions, to scavengers which react effectively with thermal hydrogen atoms, radicals and ions.[4,8] Further, the observed distribution of labeled products has been interpreted as largely resulting from the decomposition of an intermediate containing the T atom plus a single molecule, in both the gaseous phase[7] and condensed phases.[4] These observations are confirmed and extended by the experiments reported here and give a clearer picture of the nature of the "hot" reactions.

Pressure Effect on Reaction Products.—In previous studies, especially those of Wolfgang, *et al.*, on methane,[6,7] experiments run at widely different pressures have not shown any differences in distribution of radioactivity among the products, nor

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[18] J. K. Lee, Burdon Musgrave and F. S. Rowland, This Journal, **81**, 3803 (1959).

would such changes be expected if the recoil tritium reaction is much faster than mean collision times in the 0.1 to 2.0 atmosphere pressure range. However, the free radicals formed by thermal addition of hydrogen atoms to butenes have a lifetime of about 10^{-7} second[19]; when formed by thermal pyrolysis, the radical lifetimes are much longer still and often react with other radicals without decomposition. Accordingly, we have in addition run measurements of radioactivity distribution as a function of pressure with *trans*-butene-2, *cis*-butene-2, isobutylene and propylene, as shown in Tables I–IV. The butenes show definite changes in product distribution with pressure, most clearly with *trans*-butene-2 because of the much larger range of pressures investigated.[20]

Very excited *sec*-butyl radicals decompose rapidly with the loss of $CH_3\cdot$ to form propylene or of H to form one of the butenes.[21] Less excited radicals will require longer to decompose and will more often lead to labeled propylene because of the lower activation energy for loss of a methyl radical than a hydrogen atom. The decrease in propylene activity with increased pressure is consistent with collisional deactivation of *sec*-butyl radicals; the deactivated radicals then react to form *n*-butane or are scavenged by nitric oxide, depending on the system. The slight decrease in butene-1 and steady increase in *n*-butane at higher pressures is also consistent with a shorter mean time before possible deactivating collisions. The absence of an observed pressure effect with propylene and isobutylene (except the HT yield of the latter), and the magnitude of the effect with the butene-2 molecules, indicate that all or most of the "hot" reactions in these systems are completed before collision with another gas molecule.

Relative Reactivity of Saturated and Unsaturated Positions.—A high kinetic energy tritium atom reacts with comparable ease with both saturated and unsaturated positions, as shown in the mixed propane–*trans*-butene-2 irradiation of Table V. The specific radioactivities of the two parent molecules are similar, although relative rates of exchange with thermal deuterium atoms differ by more than a factor of 1000.[21] The lack of discrimination in reaction by recoil tritium is a direct result of the high kinetic energy—the recoil atom carries sufficient energy to overcome activation energy barriers, and the course of the reaction is then determined by "steric" factors, somewhat analogous to the p values of kinetic collision theory.[22]

Similarly, little preference is shown among possible intramolecular reactions. The competition between saturated and unsaturated positions in *trans*-butene-2 can be approximately analyzed by reactions 1 to 7 below, as shown in Table VII. Reaction with both positions is clearly important.[23]

TABLE VII

INTRAMOLECULAR COMPARISON OF REACTIVITY OF CARBON ATOMS IN *trans*-BUTENE-2[23]

Compound	Satur. carbon	Unsatur. carbon	Total
trans-Butene-2	24.2[20]	1.7	25.9%
cis-Butene-2		1.7	1.7%
Butene-1		4.5	4.5%
Propylene		15.0	15.0%
Methane	2.4		2.4%
	26.6%	22.9%	

Yields of Some Specific Products. **(a) Lack of Carbon Skeletal Isomerization.**—The yields of isobutylene and isobutane from T reactions with straight chain butenes are too low to be measured. There is also no isomerization to straight chain butenes or *n*-butane in reactions with isobutylene. The amounts of energy equilibrated throughout the molecule cannot be very large, or some skeletal isomerization should be expected. Failure to equilibrate large amounts of energy could result either from a very fast reaction without equilibration or from comparatively low energy reactions. The latter is apparently the case with the *sec*-butyl radicals from butene-2.

(b) Unsaturated "Hot" Products from Propane.—The yields of labeled ethylene and propylene from reactions with propane show positive evidence that a small percentage of the "hot" reactions with a saturated hydrocarbon cause the loss of more than one group in decomposition, thus producing labeled unsaturated molecules. A small percentage of reactions with olefins proceed in similar fashion to produce still more unsaturated molecules, *e.g.*, allene and methylacetylene from propylene. These labeled products usually contain about 1 or 2% of the total tritium activity and presumably result from reactions that have involved especially high initial kinetic energy of the tritium atom. These products are similar to the $CH_3\cdot$, $CH_2:$, etc., from methane[7] and CH_3CTO from ethyl alcohol.[4]

(c) Thermal Reaction Products.—Those recoil tritium atoms which fail to react in their collisions at high energy will undergo further collisions at lower energies until eventually a stable bond is formed. As the kinetic energy falls, the relative probability of different reactions may change drastically. All tritium reactions with propane except hydrogen abstraction to form HT become very improbable at lower energies. Both addition and abstraction reactions can proceed down to thermal energies in unsaturated systems, with the result that much less HT is produced than in the saturated systems.

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(19) B. S. Rabinovitch and R. W. Diesen, *J. Chem. Phys.*, **30**, 735 (1959).

(20) The reactions of Table II also involve changing ratios of He^3 to *trans*-butene-2, as well as the pressure change. However, a very much larger change in helium-*trans*-butene-2 ratio is required before the relative propylene activity begins to rise from that effect, as shown in Table III. The isotopic difference between He^3 and He^4 in elastic collisions with tritium is very small and can be neglected.

The *trans*-butene-2 activities of Table II include perhaps 8–10% isopentane, so the true ratio of propylene to parent is somewhat higher than indicated in the Table. The trends with pressure will depend only slightly on this change; no isopentane is present in the nitric oxide data of Table III or in the variation with *cis*-butene-2 in Table I.

(21) A. F. Trotman-Dickenson, "Gas Kinetics," Butterworth Scientific Publications, London, 1955.

(22) See P. Estrup and R. Wolfgang, THIS JOURNAL, **82**, 2661 (1960).

(23) The assumption of equal *cis*- and *trans*-butene-2 from reactions 2a plus 7 probably introduces some error. The source of the H atoms in "hot" HT is not yet known.

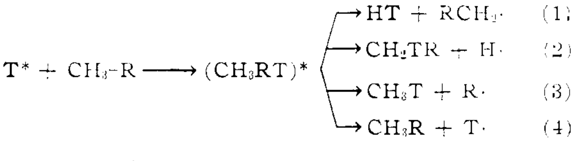
Similarly, some of the labeled reactive fragments ($CH_2T\cdot$, etc.) from higher energy reactions will react as thermal radicals, usually leading to products of higher molecular weight than the parent compound. These thermalized radicals, especially in saturated systems, often react with other radicals or fragments, rather than with stable molecules, and hence show some dependence on the radiation intensity during irradiation.

Radical scavengers, such as NO, O_2 or I_2, preferentially react with these thermalized atoms and radicals and prevent the formation of the usual thermal products. The *trans*-butene-2 in Table V served as an effective scavenger for those reactive species which form labeled isobutane and some of the HT when produced in propane alone. Noticeably higher yields of butene-1 are obtained from *trans*-butene-2 in the presence of nitric oxide than in the olefin alone (Tables II and III). The excess butene-1 is produced by reaction of *sec*-butyl radicals with NO; in its absence, the same radicals eventually form *n*-butane or isopentane.

(d) **Dimers.**—The saturated dimers from propylene do not show much specificity of reaction in their formation of the three hexanes, 2,3-dimethylbutane, 2-methylpentane and *n*-hexane, as all are formed in comparable amounts. Only 2,2-dimethylbutane, which would require either a skeletal carbon rearrangement or an additional reaction is absent. On the other hand, the dimers from propane, present in much lower yield, do not show *n*-hexane but do show 2,3-dimethylbutane and 2-methylpentane. The lower yield of dimer and saturated hydrocarbons is to be expected since the attack of a propyl radical on propylene is much easier than the corresponding reaction with propane. With saturated parent molecules, much of the dimer formation may come from reaction with species produced by radiation damage. Among the other saturated molecules of molecular weight greater than the parent, it is interesting to note that the percentage of labeled isopentane is always considerably higher than the corresponding percentage of *n*-pentane.

The Mechanism of Hot Reactions.—The offered hypotheses (a) and (b) describe the reactions of recoil tritium observed in these and previous experiments:

(a) **Saturated Carbon Reactions.**—An energetic tritium atom reacting at a saturated carbon position in a molecule passes through a short-lived ($<10^{-9}$ second) transition state which then decomposes by reactions

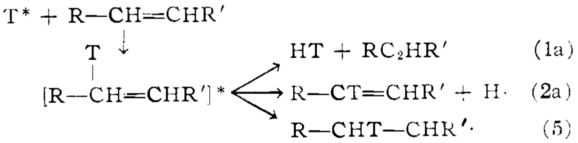


$$T^* + CH_3\text{-}R \longrightarrow (CH_3RT)^* \begin{cases} \rightarrow HT + RCH_2\cdot & (1) \\ \rightarrow CH_2TR + H\cdot & (2) \\ \rightarrow CH_3T + R\cdot & (3) \\ \rightarrow CH_3R + T\cdot & (4) \end{cases}$$

Reaction 4 leads to an energetically degraded tritium atom, which then reacts again at the lower energy. As the kinetic energy of the tritium atom approaches thermal energies, the abstraction reaction 1 to form HT predominates in the absence of efficient free-radical scavengers. The "hot" products observed from saturated systems are chiefly HT and the labeled parent molecule, indicating that reactions 1 and 2 are more likely than the loss of an R· group by reaction 3. Approximate computations of yields from saturated molecules and from saturated positions of unsaturated molecules indicate that k_2/k_3 is about 2 per available bond for C–H/C–C.

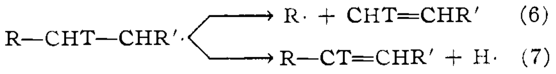
Recoil tritium experiments in the solid state on compounds with asymmetric carbon atoms suggest that the geometry of the transition state is such that reaction 2 takes place with almost complete retention of configuration.[24] Confirmation by gas-phase experimental work is still very desirable. Reaction 3 also proceeds in non-hydrocarbons when R is $-NO_2$, $-NH_2$, –OH, –COOH, halogens, etc.[9]

(b) **Unsaturated Carbon Positions.**—The energetic reaction of a tritium atom with an unsaturated carbon position is different from the saturated position especially in the relatively high yields of a labeled free radical as a "hot" product, as shown in reaction 5; chemically stable radioactive products are formed in "hot" reactions 1a and 2a.



$$\begin{array}{l} T^* + R\text{—}CH\text{=}CHR' \\ \qquad\downarrow \\ [R\text{—}\overset{T}{C}H\text{=}CHR']^* \begin{cases} \rightarrow HT + RC_2HR' & (1a) \\ \rightarrow R\text{—}CT\text{=}CHR' + H\cdot & (2a) \\ \rightarrow R\text{—}CHT\text{—}CHR'\cdot & (5) \end{cases} \end{array}$$

The free radical product of reaction 5, excited both by the kinetic energy of the recoil atom and by the exothermicity of the addition reaction, equilibrates this energy and decomposes to a stable molecule and a radical, as



$$R\text{—}CHT\text{—}CHR'\cdot \begin{cases} \longrightarrow R\cdot + CHT\text{=}CHR' & (6) \\ \longrightarrow R\text{—}CT\text{=}CHR' + H\cdot & (7) \end{cases}$$

As Urch and Wolfgang have observed,[10] the stable labeled products from a wide variety of olefinic compounds are those corresponding to the high-temperature thermal decomposition of radicals as in (6) and (7).

At the energies at which recoil tritium atoms react with most hydrocarbons, the saturated and unsaturated positions participate about equally well. Since the activation energy is higher for reaction with the former, dilutions of mixtures with large amounts of helium moderator should lead eventually to preferential reaction with the unsaturated position. Such experiments may help to establish the energy range in which the bulk of recoil tritium reactions are actually occurring.

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[24] H. Keller and F. S. Rowland, *J. Phys. Chem.*, **62**, 1373 (1958); J. Kay, R. P. Malsan and F. S. Rowland, This Journal, **81**, 5050 (1959).